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CLEAN
WATER

METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES

1971

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Cincinnati, Ohio

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This handbook describes chemical analytical procedures to be used in Water Quality Office (WQO) laboratories. Method selection was based on the following criteria: (1) The method should measure the desired constituent with precision and accuracy sufficient to meet the data needs of WQO in the presence of the interferences normally encountered in polluted waters. (2) The procedures should utilize the equipment and skills normally available in the typical water pollution control laboratory. (3) The selected methods should be in use in many laboratories or have been sufficiently tested to establish their validity. (4) The methods should be sufficiently rapid to permit routine use for the examination of a large number of samples. Except where noted under 'Scope and Application' for each constituent, the methods can be used for the measurement of the indicated constituent in both water and wastewaters and in both saline and fresh water samples. Instrumental methods have been selected in preference to manual procedures because of the improved speed, precision, and accuracy. Procedures for the Technicon AutoAnalyzer have been included for laboratories having thiseequipment available. (Mortland-Battelle)

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17b. Identifiers
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Abstractor John E. Mortland

Institution Analytical Quality Control Lab., EPA, Cincinnati

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METHODS FOR CHEMICAL ANALYSIS
OF
WATER AND WASTES

1971

ENVIRONMENTAL PROTECTION AGENCY
Water Quality Office
Analytical Quality Control Laboratory
1014 Broadway
Cincinnati, Ohio 45202

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PREFACE

This manual describes the analytical procedures selected for use in Water Quality Office laboratories for the chemical analysis of water and waste samples. The methods were chosen by a committee of senior chemists from within the Office, using Standard Methods for the Examination of Water and Wastewater, 13th Edition (1971) and ASTM Standards, Part 23, Water; Atmospheric Analysis (1970), and current water pollution control literature as basic references. When necessary, methods derived from these sources have been modified or replaced to more adequately meet the needs of the Office.

In order to provide reliable water quality and waste constituent data for use by the Office, these procedures will be used in all Office laboratories except under very unusual circumstances. Other agencies and individuals are encouraged to use these methods, in the interest of uniformity throughout the water pollution control effort.

David D. Dominic

David D. Dominick
Acting Commissioner
Water Quality

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INTRODUCTION

This 1971 edition of "Methods for Chemical Analysis of Water and Wastes" describes chemical analytical procedures to be used in Water Quality Office (WQO) laboratories. The methods were chosen through the combined efforts of the Regional Analytical Quality Control (AQC) Coordinators, Laboratory Quality Control Officers, and other senior chemists in both federal and state laboratories. Method selection was based on the following criteria:

(1) The method should measure the desired constituent with precision and accuracy sufficient to meet the data needs of WQO in the presence of the interferences normally encountered in polluted waters.

(2) The procedures should utilize the equipment and skills normally available in the typical water pollution control laboratory.

(3) The selected methods are in use in many laboratories or have been sufficiently tested to establish their validity.

(4) The methods should be sufficiently rapid to permit routine use for the examination of a large number of samples.

Except where noted under "Scope and Application" for each constituent, the methods can be used for the measurement of the indicated constituent in both water and wastewaters and in both saline and fresh water samples.

Instrumental methods have been selected in preference to manual procedures because of the improved speed, precision, and accuracy. Procedures for the Technicon AutoAnalyzer have been included for laboratories having this equipment available.

Precision and accuracy statements have been derived from inter-laboratory studies conducted by the Methods and Performance Activity, Analytical Quality Control Laboratory, WQO; the American Society for Testing Materials; or the Analytical Reference Service of the Public Health Service, DHEW.

Specific instructions for the handling and preservation of samples cannot be given because of the wide variability in types of samples and local sampling situations. However, certain general principles should be followed. Wherever possible, the sampling program should be designed to provide for the shortest possible interval between sample collection and analysis. Positive steps should be taken to maintain both the concentration and the physical state of the constituents to be measured. Where both total and dissolved concentrations are to be determined, the dissolved concentration is the amount present after filtration through a 0.45 membrane filter. When the dissolved concentration is to be determined, filtration should be carried out as soon as possible after collection of the sample, preferably in the field. Where field filtration is not practical, the sample should be filtered as soon as it is received in the laboratory.

In situations where the interval between sample collection and analysis is long enough to produce significant changes in either the concentration or the physical state of the constituent to be measured, the preservatives listed in Table II are recommended.

Although every effort has been made to select methods which are applicable to the widest range of sample types, significant interferences may be encountered in certain isolated samples. In these situations, the analyst should define the nature of the interference with the method herein and bring this information to the attention of the Analytical Quality Control Laboratory through the appropriate Regional AQC Coordinator. Recommendations for alternative procedures will be made and modification of the method will be developed to overcome the interferences.

Regional Analytical Quality Control Coordinators

Francis T. Brezenski, AQC Coordinator
Water Quality Office, EPA
Hudson-Delaware Basins Office
Edison, New Jersey 08817

R. Kenneth Tinsley, AQC Coordinator
Water Quality Office, EPA
918 Emmet Street
Charlottesville, Virginia 22901

James H. Finger, AQC Coordinator
Water Quality Office, EPA
Southeast Water Laboratory
College Station Road
Athens, Georgia 30601

LeRoy E. Scarce, AQC Coordinator
Water Quality Office, EPA
1819 West Pershing Road
Chicago, Illinois 60605

Carl M. Walter, AQC Coordinator
Water Quality Office, EPA
911 Walnut Street, Room 702
Kansas City, Missouri 64106

Bobby G. Benefield, AQC Coordinator
Water Quality Office, EPA
Kerr Water Research Center
P.O. Box 1198
Ada, Oklahoma 74820

Daniel F. Krawczyk, AQC Coordinator
Water Quality Office, EPA
Pacific Northwest Water Laboratory
200 South 35th Street
Corvallis, Oregon 97330

Donald B. Mausshardt, AQC Coordinator
Water Quality Office, EPA
Phelan Building, 760 Market Street
San Francisco, California 94102

Robert L. Booth, AQC Coordinator
Water Quality Office, EPA
Analytical Quality Control Laboratory
1014 Broadway
Cincinnati, Ohio 45202

SAMPLE PRESERVATION

Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source.

The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. Biological changes taking place in a sample may change the state of an element or a radical to a different state. Soluble constituents may be converted to organically bound material in cell structures, or cell lysis may result in release of cellular materials into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition.

Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes and (3) reduce volatility of constituents.

Preservation methods are generally limited to pH control, chemical addition, refrigeration, and freezing. Table 1 shows the various preservatives that may be used to retard changes in samples.

Table 1

Preservative	Action	Applicable to:
$HgCl_2$	Bacterial Inhibitor	Nitrogen forms, Phosphorus forms
Acid (HNO_3)	Metals solvent, prevents precipitation	Metals
Acid (H_2SO_4)	Bacterial Inhibitor	Organic samples (COD, oil & grease, organic carbon, etc.)
	Salt formation with organic bases	Ammonia, amines
Alkali (NaOH)	Salt formation with volatile compounds	Cyanides, organic acids
Refrigeration or freezing	Bacterial Inhibitor	Acidity - alkalinity, organic materials, BOD, color, odor, organic P, organic N, carbon, etc., biological organisms (coliform, etc.)

In summary, refrigeration at temperatures near freezing or below is the best preservation technique available, but is not applicable to all types of samples.

The recommended choice of preservatives for various constituents is given in Table 2. These choices are based on the accompanying references and on information supplied by various Regional Analytical Quality Control Coordinators.

Table 2 - Sample Preservation

Parameter	Preservative	Maximum Holding Period
Acidity-Alkalinity	Refrigeration at 4°C	24 hours
Biochemical Oxygen Demand	Refrigeration at 4°C	6 hours
Calcium	None required	7 days
Chemical Oxygen Demand	2 ml H_2SO_4 per liter	7 days
Chloride	None required	7 days
Color	Refrigeration at 4°C	24 hours
Cyanide	NaOH to pH 10	24 hours
Dissolved Oxygen	Determine on site	No holding
Fluoride	None required	7 days
Hardness	None required	7 days
Metals, Total	5 ml HNO_3 per liter	6 months
Metals, Dissolved	Filtrate: 3 ml 1:1 HNO_3 per liter	6 months
Nitrogen, Ammonia	40 mg $HgCl_2$* per liter - 4°C	7 days
Nitrogen, Kjeldahl	40 mg $HgCl_2$* per liter - 4°C	Unstable
Nitrogen, Nitrate-Nitrite	40 mg $HgCl_2$* per liter - 4°C	7 days
Oil and Grease	2 ml H_2SO_4 per liter - 4°C	24 hours
Organic Carbon	2 ml H_2SO_4 per liter (pH 2)	7 days
pH	Determine on site	No holding
Phenolics	1.0 g $CuSO_4$/1 + H_3PO_4 to pH 4.0 - 4°C	24 hours
Phosphorus	40 mg $HgCl_2$* per liter - 4°C	7 days

*Disposal of mercury-containing samples is a recognized problem; research investigations are under way to replace it as a preservative.

Table 2 - Sample Preservation
(Continued)

Parameter	Preservative	Maximum Holding Period
Solids	None available	7 days
Specific Conductance	None required	7 days
Sulfate	Refrigeration at 4°C	7 days
Sulfide	2 ml Zn acetate per liter	7 days
Threshold Odor	Refrigeration at 4°C	24 hours
Turbidity	None available	7 days

References:

Jenkins, David, "A Study of Methods Suitable for the Analysis and Preservation of Phosphorus Forms in an Estuarine Environment." Report for the Central Pacific River Basins Project, Southwest Region, FWPCA (1965).

Jenkins, David, "A Study of Method for the Analysis and Preservation of Nitrogen Forms in an Estuarine Environment." Report for the Central Pacific River Basins Project, Southwest Region, FWPCA (1965).

Howe, L. H. and Holley, C. W. "Comparisons of Mercury (II) Chloride and Sulfuric Acid as Preservatives for Nitrogen Forms in Water Samples." Env. Sci. & Tech. 3:478 (1969).

ACIDITY

STORET NO. 00435

1. Scope and Application

1.1 The method recommended is identical to the procedure described in ASTM Standards, Part 23, pp 155-158, except that the sample is titrated to a final pH of 8.3 and results reported as mg/l $CaCO_3$.

1.2 This method is not applicable to analysis of acid samples from mine drainage. It is the decision of the AQC staff to delay the method selection for measurement of acidity in acid mine drainage samples until such time that a more comprehensive review of the problem can be made.

1.3 Methods for analysis of mine drainage samples for all constituents contributing to acidity of such samples may be selected at the option of the respective laboratory directors.

2. Calculation

2.1 Acidity is reported as calcium carbonate ($CaCO_3$) according to the following formula:

$$\text{Acidity as mg/l } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{ml sample}}$$

where:

A = ml of base used for titration

N = normality of base

3. Precision and Accuracy

3.1 Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate with the following results:

Increment as Acidity mg/l, $CaCO_3$	Precision as Standard Deviation mg P/liter	Accuracy as Bias, %	Accuracy as Bias, mg P/Liter
20	1.79	+2.77	+.55
21	1.73	+0.52	+.11

(FWPCA Method Study 1, Mineral and Physical Analyses)

ALKALINITY

STORET Number: 00410

1. Scope and Application

1.1 This method is applicable to drinking waters and surface waters, domestic and industrial wastes, and saline waters.

1.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 ml.

1.3 Automated titrimetric analysis is equivalent.

2. Summary of Method

2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.

3. Comments

3.1 The sample must be analyzed as soon as practical; preferably, within a few hours. Do not open sample bottle before analyses.

3.2 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.

3.3 Oil and greases, by coating the pH electrode, may also interfere, causing sluggish response.

4. Precision and Accuracy

4.1 Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

Increment as Alkalinity mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCO_3$	Accuracy as Bias, %	Bias, mg/liter, $CaCO_3$
8	1.27	+10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	- 8.19	-9.3
119	5.36	- 7.42	-8.8

(FWPCA Method Study 1, Mineral and Physical Analyses)

4.2 In a single laboratory (AQC), using surface water samples at an average concentration of 122 mg $CaCO_3$/l, the standard deviation was ± 3.

5. Reference

5.1 The procedure to be used for this determination is found in:
Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 52, Method 102 (1971).
ASTM Standards, Part 23, Water; Atmospheric Analysis, p. 154, Method D-1067 (1970).

TOTAL ALKALINITY

(Automated Methyl Orange Method)

STORET NO. 00410

1. Scope and Application

1.1 This automated method is applicable to surface and saline waters. The applicable range is 10 to 200 mg/l as $CaCO_3$.

2. Summary of Method

2.1 Methyl orange is used as the indicator in this method because its pH range is in the same range as the equivalence point for total alkalinity, and it has a distinct color change that can be easily measured. The methyl orange is dissolved in a weak buffer at a pH of 3.1, just below the equivalence point, so that any addition of alkalinity causes a loss of color directly proportional to the amount of alkalinity.

3. Sample Handling and Preservation

3.1 Sample should be refrigerated at 4°C and run as soon as practical.

4. Interferences

4.1 No significant interferences.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I.

5.1.2 Manifold.

5.1.3 Proportioning pump.

5.1.4 Colorimeter equipped with 15 mm tubular flow cell and 550 nm filters.

5.1.5 Recorder equipped with range expander.

6. Reagents

6.1 Methyl Orange: Dissolve 0.125 g of methyl orange in 1 liter of distilled water.

6.2 pH 3.1 Buffer: Dissolve 5.1047 g of potassium acid phthalate in distilled water and add 87.6 ml 0.1 N HCl and dilute to 1 liter. Stable for one week.

6.3 Methyl Orange-Buffered Indicator: Add 1.0 liter of pH 3.1 buffer to 200 ml methyl orange solution and mix well. Stable for 24 hours.

6.4 Stock Solution: Dissolve 1.060 g of anhydrous sodium carbonate (oven-dried at 140°C for 1 hour) in distilled water and dilute to 1.0 liter. 1.0 ml = 1.00 mg $CaCO_3$.

6.4.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l as $CaCO_3$
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
18.0	180
20.0	200

7. Procedure

7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings on sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (AQC), using surface water samples at concentrations of 15, 57, 154, and 193 mg/l as $CaCO_3$, the standard deviation was ±0.5.

9.2 In a single laboratory (AQC), using surface water samples at concentrations of 31 and 149 mg/l as $CaCO_3$, recoveries were 100% and 99%, respectively.

References

1. Technicon AutoAnalyzer Methodology, Bulletin 1261, Technicon Controls, Inc., Chauncey, N.Y. (1961).
2. Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 52, Method 102 (1971).

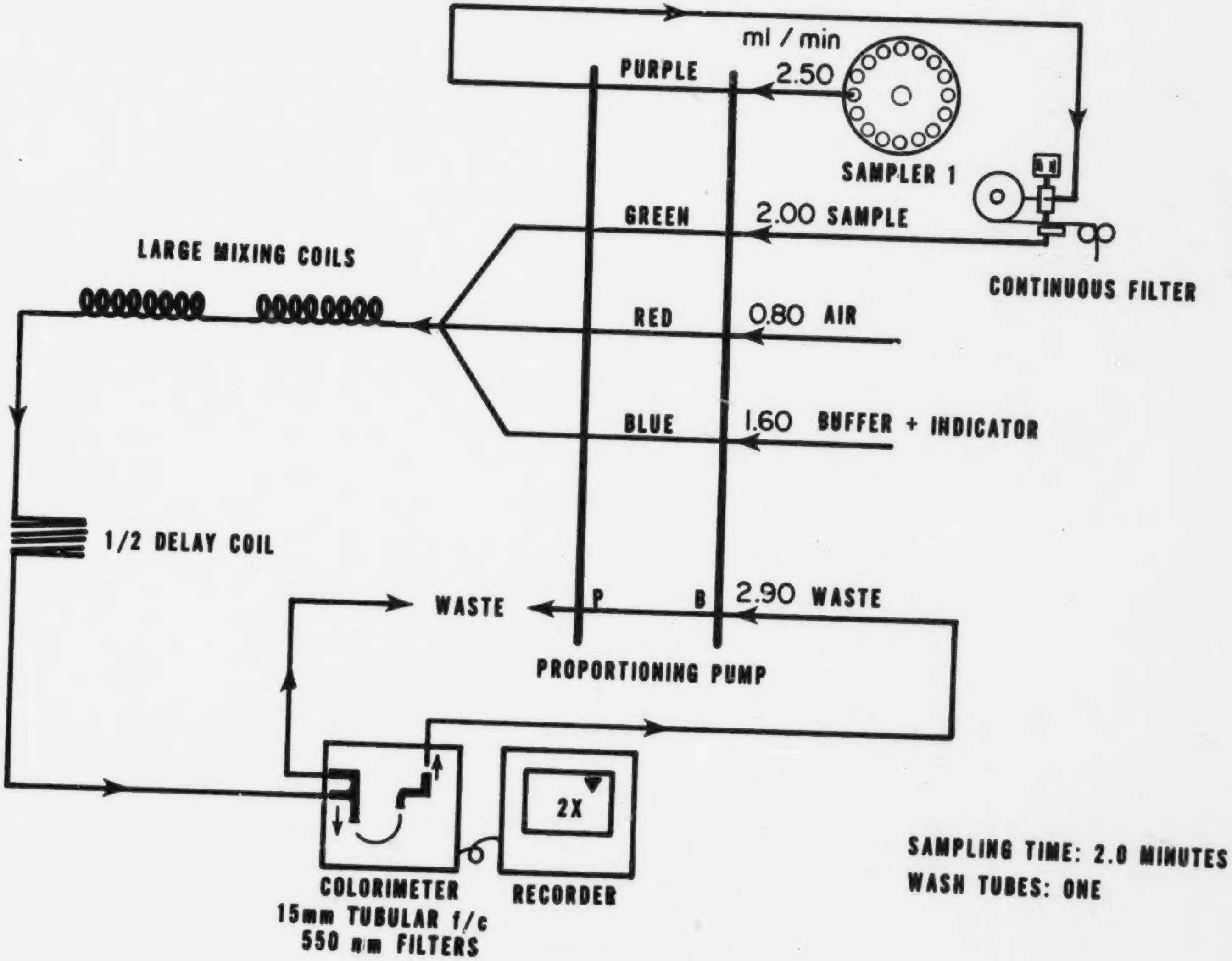
ml / min
PURPLE
2.50
SAMPLER 1
GREEN
2.00 SAMPLE
CONTINUOUS FILTER
LARGE MIXING COILS
RED
0.80 AIR
BLUE
1.60 BUFFER + INDICATOR
1/2 DELAY COIL
WASTE
P
B
2.90 WASTE
PROPORTIONING PUMP
2X
COLORIMETER
15mm TUBULAR f/c
550 nm FILTERS
RECORDER
SAMPLING TIME: 2.0 MINUTES
WASH TUBES: ONE

FIGURE 1. ALKALINITY MANIFOLD

ARSENIC

STORET NO. _____ (Total)
01000 (Inorganic)

1. Scope and Application

1.1 The silver diethyldithiocarbamate method determines inorganic arsenic when present in concentrations at or above 10 µg/l. The method is applicable to most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver.

1.2 Difficulties may be encountered with certain industrial waste materials containing volatile substances. High sulfur content of wastes may exceed removal capacity of the lead acetate scrubber.

2. Summary of Method

2.1 Arsenic in the sample is reduced to arsine, AsH_3, in acid solution in a hydrogen generator. The arsine is passed through a scrubber to remove sulfide and is absorbed in a solution of silver diethyldithiocarbamate dissolved in pyridine. The red complex thus formed is measured in a spectrophotometer at 535 nm.

3. Comments

3.1 In analyzing most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of arsenic to establish adequate recovery.

3.2 It is essential that the system be air-tight during evolution of the arsine, to avoid losses.

3.3 If concentration of sample and oxidation of any organic matter is desired to measure organically-bound arsenic, refer to Standard Methods, 13th Ed., Method 104B, p 65, Procedure 4.a (1971).

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4. Precision and Accuracy

4.1 A synthetic unknown sample containing 40 µg/l, as As, with other metals was analyzed in 46 laboratories. Relative standard deviation was 13.8% and relative error was 0%.

5. Reference

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 62, Method 104A (1971).

BIOCHEMICAL OXYGEN DEMAND

STORET No: 00310

1. Scope and Application

1.1 The biochemical oxygen demand test (BOD) is used for determining the relative oxygen requirements of municipal and industrial wastewaters. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria for the design of wastewater treatment plants.

1.2 The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20°C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

2. Summary of Method

The sample of waste, or an appropriate dilution, is incubated for 5 days at 20°C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

3. Comments

3.1 Because of the effect of local conditions, types of samples to be tested, and the variabilities in bioassay procedures, no specific standard test for BOD has been selected by the Water Quality Office.

3.2 Determination of dissolved oxygen in the BOD test may be made by use of either the Modified Winkler with Full-Bottle Technique (Pg. 53) or the Probe Method (Pg. 60) in this manual.

3.3 Additional information relating to oxygen demanding characteristics of wastewaters can be gained by applying the Total Organic Carbon and Chemical Oxygen Demand tests (see pp 221-229 and 17-28, respectively).

4. Precision and Accuracy

4.1 Seventy-seven analysts in fifty-three laboratories analyzed natural water samples plus an exact increment of biodegradable organic compounds. At a mean value of 194 mg/l BOD, the standard deviation was ±40 mg/l.

4.2 There is no acceptable procedure for determining the accuracy of the BOD test.

5. References

The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, P. 489, Method 219 (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, P. 712, Method D 2329-68 (1970).

CHEMICAL OXYGEN DEMAND

STORET No: 00340

1. Scope and Application

1.1 This method determines the quantity of oxygen required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time.

1.2 Since the test utilizes a rigorous chemical oxidation rather than a biological process, the result has no defineable relationship to the BOD of the waste. The test result should be considered as an independent measurement of organic matter in the sample, rather than as a substitute for the BOD test.

1.3 The method can be applied to domestic and industrial waste samples having an organic carbon concentration greater than 15 mg/l. For lower concentrations of carbon such as in surface water samples, the Low Level Modification, Pg. 19, should be used. When the chloride concentration of the sample exceeds 2000 mg/l, the modification for saline waters, pg. 24, is required.

2. Summary of Method

2.1 Organic substances in the sample are oxidized by potassium dichromate in 50% sulfuric acid solution at reflux temperature. Silver sulfate is used as a catalyst and mercuric sulfate is added to remove chloride interference. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as an indicator.

3. Comments

3.1 To reduce loss of volatile organics, the flask should be cooled during addition of the sulfuric acid solution.

4. Precision and Accuracy

4.1 Eighty-nine analysts in fifty-eight laboratories analyzed a distilled water solution containing oxidizable organic material equivalent to 270 mg/l COD. The standard deviation was ±27.5 mg/l COD and the mean recovery was 96% of the true value.

5. References

The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, P. 495 Method 220 (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, P. 246 Method D 1252-67 (1970).

CHEMICAL OXYGEN DEMAND

(Low Level)

STORET NO. 00335

1. Scope and Application

1.1 The scope of this modification of the Chemical Oxygen Demand (COD) test is the same as for the high level test. It is applicable to the analysis of surface waters, domestic and industrial wastes with low demand characteristics.

1.2 This method (low level) is applicable for samples having a COD in the range of 5-50 mg/l COD.

2. Summary of Method

2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid solution. The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.

3. Sampling and Preservation

3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.

3.3 Samples may be preserved with sulfuric acid at a rate of 2 ml of conc. H_2SO_4 per liter of sample.

4. Interferences

4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.

4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.

4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.

4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.

4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine and estuarine samples.

5. Apparatus

5.1 Reflux apparatus - Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. Reagents

6.1 Distilled water. Special precautions should be taken to insure that distilled water used in this test be low in organic matter.

6.2 Standard potassium dichromate solution (0.025 N) - Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103°C for two hours, in distilled water and dilute to 1.0 1. Mix this solution thoroughly then dilute 100 ml to 1.0 1 with distilled water.

6.3 Sulfuric acid reagent - Conc. H_2SO_4 containing 23.5 g silver sulfate, Ag_2SO_4, per 9 lb. bottle (one to two days required for dissolution).

6.4 Standard ferrous ammonium sulfate (0.025 N) - Dissolve 9.8 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4, cool and dilute to 1.0 l. Dilute 100 ml of this solution to 1.0 l with distilled water. This solution must be standardized daily against $K_2Cr_2O_7$ solution.

6.4.1 Standardization - To 15 ml of distilled water add 10 ml of 0.025 N $Kr_2Cr_2O_7$ solution. Add 20 ml of H_2SO_4 and cool. Titrate with ferrous ammonium sulfate using 1 drop of ferroin indicator. The color change is sharp, going from blue-green to reddish-brown.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)(0.025)}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

6.5 Mercuric sulfate - Powdered $HgSO_4$.

6.6 Phenanthroline ferrous sulfate (ferroin) indicator solution - Dissolve 1.48 g of 1-10-(ortho)-phenanthroline monohydrate, together with 0.70 g of $FeSO_4.7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.7 Silver sulfate - Powdered Ag_2SO_4.

6.8 Sulfuric acid (sp. gr. 1.84) - Concentrated H_2SO_4.

7. Procedure

7.1 Place several boiling stones in the reflux flask, followed by 1 g of $HgSO_4$. Add 5.0 ml conc. H_2SO_4 (6.8); swirl until mercuric sulfate has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0 ml of 0.025 N $K_2Cr_2O_7$. Now add 70.0 ml of sulfuric acid-silver sulfate solution (6.3) to the cooled reflux flask, again using slow addition with swirling motion.

7.2 With the reflux flask still in the ice bath, place 50.0 ml of sample or a sample aliquot diluted to 50.0 ml into the reflux flask. Caution: Care must be taken to assure that the contents of the flask are well mixed. If not, superheating may result, and the mixture may be blown out of the open end of the condenser. Attach the flask to the condenser and start the cooling water.

7.3 Apply heat to the flask and reflux for 2 hours. For some waste waters, the 2-hour reflux period is not necessary. The time required to give the maximum oxidation for a waste water of constant or known composition may be determined and a shorter period of refluxing may be permissible.

7.4 Allow the flask to cool and wash down the condenser with about 25 ml of water. If a round bottom flask has been used, transfer the mixture to a 500-ml Erlenmeyer flask, washing out the reflux flask 3 or 4 times with water. Dilute the acid solution to about 300 ml with water and allow the solution to cool to about room temperature. Add 8 to 10 drops of ferroin indicator to the solution and titrate the excess dichromate with 0.025 N ferrous ammonium sulfate solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.

7.5 Blank - Simultaneously run a blank determination following the details given in 7.1 and 7.2, but using low COD water in place of the sample.

8. Calculation

8.1 Calculate the COD in the sample in mg/l as follows:

$$\text{COD, mg/liter} = \frac{(A - B)\ N \times 8000}{S}$$

where:

A = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the blank,

B = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the sample,

N = normality of the $Fe(NH_4)_2(SO_4)_2$ solution, and

S = milliliters of sample used for the test.

9. Precision

9.1 The precision of the low level test described in the foregoing material has not been determined by collaborative testing.

CHEMICAL OXYGEN DEMAND

(High Level for Saline Waters)

STORET NO. 00340

1. Scope and Application

1.1 When the chloride level exceeds 1000 mg/l the minimum accepted value for the COD will be 250 mg/l. COD levels which fall below this value are highly questionable because of the high chloride correction which must be made.

2. Summary of Method

2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid solution. The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.

3. Sample Handling and Preservation

3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.

3.3 Samples are preserved by the addition of 2 ml of conc. H_2SO_4 per liter of sample.

4. Interferences

4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.

4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.

4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.

4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.

4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine samples.

5. Apparatus

5.1 Reflux apparatus - Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. Reagents

6.1 Standard potassium dichromate solution, (0.25 N): Dissolve 12.2588 g of $K_2Cr_2O_7$, primary standard grade, previously dried for 2 hours at 103°C in water and dilute to 1.0 liter.

6.2 Sulfuric acid reagent: Conc. H_2SO_4 containing 23.5 g silver sulfate, Ag_2SO_4, per 9 lb. bottle (1 to 2 days required for dissolution).

6.3 Standard ferrous ammonium sulfate, 0.250 N: Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4, cool and dilute to 1.0 1. This solution must be standardized against the standard potassium dichromate solution daily.

6.3.1 Standardization: Dilute 25.0 ml of standard dichromate solution to about 250 ml with distilled water. Add 75 ml conc. sulfuric acid. Cool, then titrate with ferrous ammonium sulfate titrant, using 10 drops of ferroin indicator.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)\ (0.25)}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

6.4 Mercuric sulfate - Powdered $HgSO_4$.

6.5 Phenanthroline ferrous sulfate (ferroin) indicator solution - Dissolve 1.48 g of 1-10-(ortho)-phenanthroline monohydrate, together with 0.70 g of $FeSO_4.7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.6 Silver sulfate - Powdered Ag_2SO_4.

6.7 Sulfuric acid (sp. gr. 1.84) - Concentrated H_2SO_4.

7. Procedure

7.1 Pipet a 50 ml aliquot of sample not to exceed 800 mg/l of COD into a 500 ml, flat bottom, Erlenmeyer flask. Add 25 ml of 0.25 N $Kr_2Cr_2O_7$, then 5.0 ml of conc. H_2SO_4 (containing no chloride, based upon the mg of chloride in the sample aliquot. Swirl until all the mercuric sulfate has dissolved. Carefully add 70 ml of sulfuric acid-silver sulfate solution and gently swirl until the solution is thoroughly mixed. Glass beads should be added to the reflux mixture to prevent bumping, which can be severe and dangerous. (CAUTION: The reflux mixture must be thoroughly mixed before heat is applied. If this is not done, local heating occurs in the botton of the flask, and the mixture may be blown out of the condenser).

7.1.1 If volatile organics are present in the sample, use an Allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser, while cooling the flask, to reduce loss by volatilization.

7.2 Attach the flask to the condenser and reflux the mixture for two hours.

7.3 Cool, and wash down the interior of the condenser with 25 ml of distilled water. Disconnect the condenser and wash the flask and condenser joint with 25 ml of distilled water. Remove the condenser and carefully add to the flask 175 ml of distilled water so that the total volume is 350 ml. Cool to room temperature.

7.4 Titrate with standard ferrous ammonium sulfate using 10 drops of ferroin indicator. (This amount must not vary from blank, sample and standardization). The color change is sharp, going from blue-green to reddish-brown and should be taken as the end point although the blue-green color may reappear within minutes.

7.5 Run a blank, using 50 ml of distilled water in place of the sample together with all reagents and subsequent treatment.

7.6 For COD values greater than 800 mg/1, a smaller aliquot of sample should be taken; however, the volume should be readjusted to 50 ml with distilled water having a chloride concentration equal to the sample.

7.7 Chloride correction* - Prepare a standard curve of COD versus mg/1 of chloride, using sodium chloride solutions of varying concentrations following exactly the procedure outlined. The chloride interval, as a minimum should be 4000 mg/l up to 20,000 mg/l chloride. Lesser intervals of greater concentrations must be run as per the requirements of the data, but in no case must extrapolation be used.

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*Burns, E. R., Marshall, C., Journal WPCF, Vol. 37, pp 1716-1721 (1965).

8. Calculation

8.1 $$\text{mg/l COD} = \frac{[(A - B)\ C \times 8000 - 50D]}{\text{ml sample}} \times 1.20$$

where:

COD = chemical oxygen demand from dichromate

A = ml $Fe(NH_4)_2(SO_4)_2$ for blank;

B = ml $Fe(NH_4)_2(SO_4)_2$ for sample;

C = normality of $Fe(NH_4)_2(SO_4)_2$;

D = chloride correction from curve (step 7.7).

1.20 = compensation factor to account for the extent of chloride oxidation which is dissimilar in systems containing organic and nonorganic material.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

CHLORIDE

STORET Number: 00940

1. Scope and Application

   1.1 This method is applicable to drinking waters and surface waters, domestic and industrial wastes, and saline waters.

   1.2 The method is, suitable for all concentration ranges of chloride content; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 10 to 20 mg Cl per 50 ml.

   1.3 Automated titration may be used.

2. Summary of Method

   2.1 Dilute mercuric nitrate solution is added to an acidified sample in the presence of mixed diphenylcarbazone - bromophenol blue indicator. The end point of the titration is the formation of the blue - violet mercury diphenylcarbazone complex.

3. Comments

   3.1 Anions and cations at concentrations normally found in surface waters do not interfere.

   3.2 Sulfites interfere. If presence is suspected, oxidize by treating 50 ml of sample with 0.5 to 1 ml of H_2O_2.

4. Precision and Accuracy

   4.1 Forty-two analysts in eighteen laboratories analyzed synthetic water samples containing exact increments of chloride, with the following results:

Increment as Chloride mg/liter	Precision as Standard Deviation mg/liter	Accuracy as Bias, %	Bias, mg/liter
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	-0.51	-0.5
382	11.7	-0.61	-2.3
398	11.8	-1.19	-4.7

(FWPCA Method Study 1, Mineral and Physical Analyses)

4.2 In a single laboratory (AQC), using surface water samples at an average concentration of 34 mg Cl/1, the standard deviation was ±1.0.

5. Reference

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 97, Method 112B (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p. 24, Method 512-67 (1970).

CHLORIDE

(Automated Ferricyanide Method)

STORET NO. 00940

1. Scope and Application

   1.1 This automated method is applicable on surface water, domestic and industrial wastes, and saline waters. The applicable range is 1 to 250 mg Cl/1. Approximately 15 samples per hour can be analyzed.

2. Summary of Method

   2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate, through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate, in concentration proportional to the original chloride concentration.

3. Sample Handling and Preservation

   3.1 No special requirements.

4. Interferences

   4.1 No significant interferences.

5. Apparatus

   5.1 Technicon AutoAnalyzer consisting of:

      5.1.1 Sampler I.

      5.1.2 Continuous filter.

      5.1.3 Manifold.

      5.1.4 Proportioning pump.

      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 480 nm filters.

      5.1.6 Recorder.

6. Reagents

   6.1 Ferric Ammonium Sulfate: Dissolve 60 g of $FeNH_4(SO_4)_2.12\ H_2O$ in approximately 500 ml distilled water. Add 355 ml of conc. HNO_3 and dilute to 1 liter with distilled water. Filter.

6.2 Saturated Mercuric Thiocyanate: Dissolve 5 g of $Hg(SCN)_2$ in 1 liter of distilled water. Decant and filter a portion of the saturated supernatant liquid to use as the reagent and refill the bottle with distilled water.

6.3 Stock Solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in distilled water. Dilute to 1 liter. 1 ml = 0.5 mg Cl^-.

6.3.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l
0.2	1.0
1.0	5.0
2.0	10
4.0	20
8.0	40
15.0	75
20.0	100
30.0	150
40.0	200
50.0	250

7. Procedure

7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1. For water samples known to be consistently low in chloride content, it is advisable to use only one distilled water intake line.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

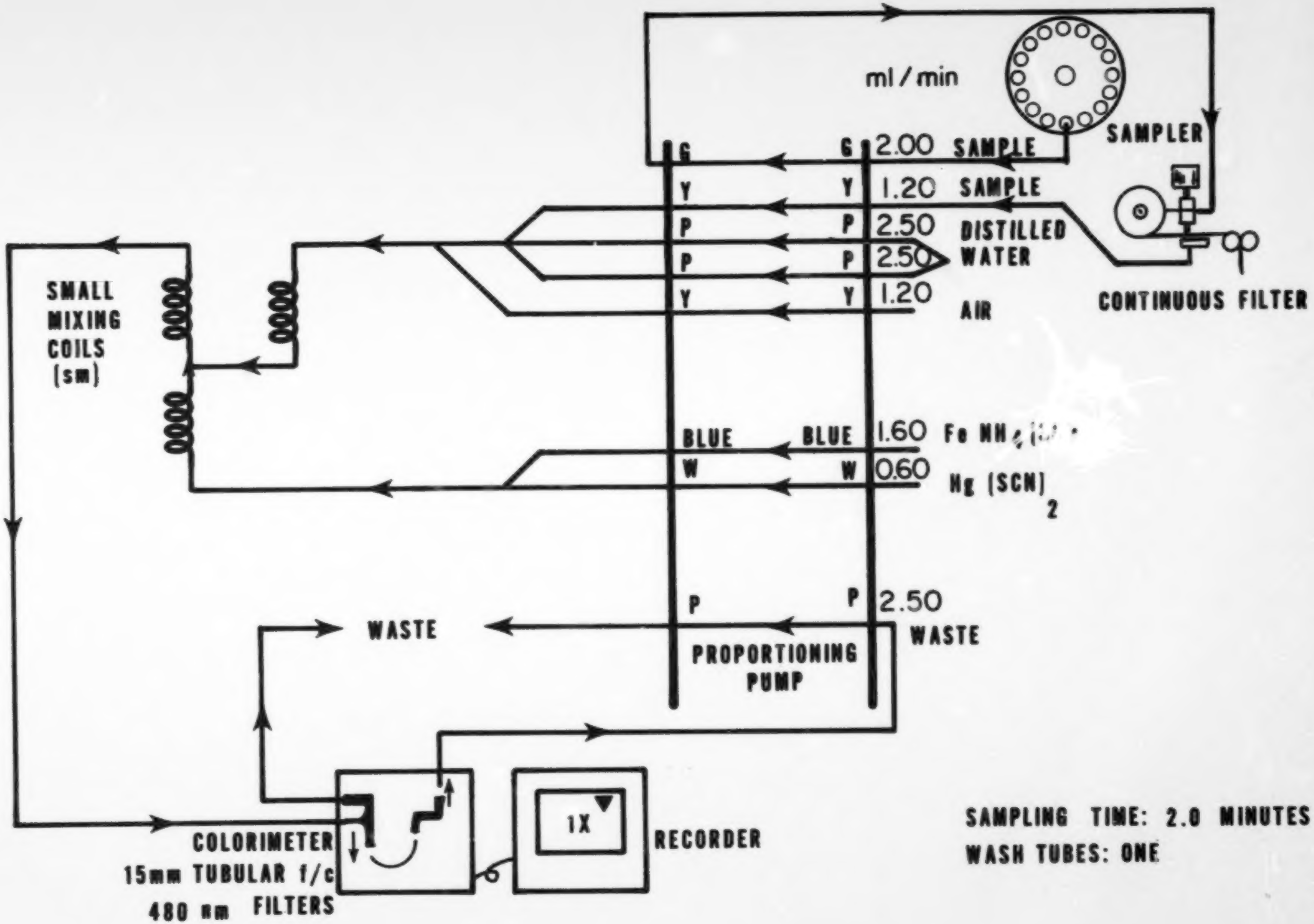
9. Precision and Accuracy

9.1 In a single laboratory, (AQC), using surface water samples at concentrations of 1, 100, and 250 mg Cl^-/1, the standard deviation was ±0.3.

9.2 In a single laboratory (AQC), using surface water samples at concentrations of 10 and 100 mg Cl/1, recoveries were 97% and 104%, respectively.

Reference

1. J. E. O'Brien, "Automatic Analysis of Chlorides in Sewage," Waste Engr., 33, 670-672 (Dec. 1962).


ml / min
SAMPLER
CONTINUOUS FILTER
G
Y
P
P
Y
G 2.00 SAMPLE
Y 1.20 SAMPLE
P 2.50 DISTILLED WATER
P 2.50
Y 1.20 AIR
SMALL MIXING COILS (sm)
BLUE
W
BLUE 1.60 Fe NH4
W 0.60 Hg (SCN)2
P
P 2.50 WASTE
WASTE
PROPORTIONING PUMP
COLORIMETER
15mm TUBULAR f/c
480 nm FILTERS
1X
RECORDER

SAMPLING TIME: 2.0 MINUTES
WASH TUBES: ONE

FIGURE 1. CHLORIDE MANIFOLD

CHLORINE REQUIREMENT

STORET NO. ________

1. Scope and Application

   1.1 This method is applicable to drinking water, surface waters, domestic and industrial wastes and saline waters. Limitations of the method are implied in paragraph 1.2, below.

   1.2 Chlorine requirement is defined as the amount of chlorine which must be added per unit volume of sample to produce a desired result under stated conditions. It is therefore applicable to control of coliform densities, destruction of certain chemical compounds and odorous materials, and establishment of specified chlorine residuals.

   1.3 Chlorine requirement is not an absolute value and cannot be used to compare results from time to time or place to place.

2. Summary of Method

   2.1 A solution of known chlorine content is added incrementally to a series of sample aliquots. At the end of the stipulated contact time or when the desired result has been achieved the residual chlorine is measured by the appropriate method.

3. Comments

   3.1 In cases where the desired result is a specified residual chlorine concentration, it is important that the same method for chlorine measurement be used for both laboratory testing and operational control.

   3.2 In reporting results all of the pertinent information must be included: the conditions of chlorination, such as pH, temperature and contact time; the method used for determining the result and the chlorine required to produce the desired result (i.e., the chlorine requirement).

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4. Precision and Accuracy

4.1 The nature of this test precludes the use of accuracy and precision statement.

5. Reference

The procedure to be used for this determination is found in:

> Standard Methods for the Examination of Water and Wastewaters, 13th Edition, pp 388-391, Method No. 205A and 205B (1971).

COLOR

STORET NO. 00080

1. Scope and Application

   1.1 The Platinum-Cobalt method is useful for measuring color of water derived from naturally occurring materials, i.e., vegetable residues such as leaves, barks, roots, humus and peat materials. The method is not applicable to color measurement on waters containing highly colored industrial wastes.

   Note - The Spectrophotometric and Tristimulus methods are useful for detecting specific color problems. The use of these methods, however, is laborious and unless determination of the hue, purity, and luminance is desired, they are of limited value.

2. Summary of Method

   2.1 Color is measured by visual comparison of the sample with platinum-cobalt standards. One unit of color is that produced by 1 mg/l platinum in the form of the chloroplatinate ion.

3. Interferences

   3.1 Since very slight amounts of turbidity interfere with the determination, samples showing visible turbidity should be clarified by centrifugation.

4. Sample Handling and Preservation

   4.1 Representative samples shall be taken in scrupulously clean glassware.

   4.2 Since biological activity may change the color characteristics of a sample, the determination should be made as soon as possible. Refrigeration at 4°C is recommended.

5. Apparatus

   5.1 Nessler tubes - Matched, tall form, 50 ml capacity.

COLOR

STORET NO. 00080

1. Scope and Application

1.1 The Platinum-Cobalt method is useful for measuring color of water derived from naturally occurring materials, i.e., vegetable residues such as leaves, barks, roots, humus and peat materials. The method is not applicable to color measurement on waters containing highly colored industrial wastes.

Note - The Spectrophotometric and Tristimulus methods are useful for detecting specific color problems. The use of these methods, however, is laborious and unless determination of the hue, purity, and luminance is desired, they are of limited value.

2. Summary of Method

2.1 Color is measured by visual comparison of the sample with platinum-cobalt standards. One unit of color is that produced by 1 mg/l platinum in the form of the chloroplatinate ion.

3. Interferences

3.1 Since very slight amounts of turbidity interfere with the determination, samples showing visible turbidity should be clarified by centrifugation.

4. Sample Handling and Preservation

4.1 Representative samples shall be taken in scrupulously clean glassware.

4.2 Since biological activity may change the color characteristics of a sample, the determination should be made as soon as possible. Refrigeration at 4°C is recommended.

5. Apparatus

5.1 Nessler tubes - Matched, tall form, 50 ml capacity.

6. Reagents

6.1 Standard chloroplatinate solution. Dissolve 1.246 g potassium chloroplatinate, K_2PtCl_6, (equivalent to 0.500 g metallic Pt) and 1 g crystalline cobaltous chloride, $CoCl_2.6H_2O$, in distilled water containing 100 ml of conc. HCl. Dilute to 1 liter with distilled water. This standard solution is equivalent to 500 color units.

7. Preparation of Standards

7.1 Prepare standards in increments from 5 to 70 units.

The following series is suggested:

ml of Standard Solution Diluted to 50.0 ml with Distilled Water	Color in Chloroplatinate Units
0.0	0
0.5	5
1.0	10
1.5	15
2.0	20
2.5	25
3.0	30
3.5	35
4.0	40
4.5	45
5.0	50
6.0	60
7.0	70

7.2 Protect these standards against evaporation and contamination by use of clean, inert stoppers.

Note - The standards also must be protected aganst the absorption of ammonia since an increase in color will result.

8. Procedure

8.1 Apparent color - Observe the color of the sample by filling a matched Nessler tube to the 50 ml mark with the water and compare with standards. This comparison is made by looking vertically downward through the tubes toward a white or specular surface placed at such an angle that light is reflected upward through the columns of liquid. If turbidity has not been removed by the procedure given in 8.2, report the color as "apparent color." If the color exceeds 70 units, dilute the sample with distilled water in known proportions until the color is within the range of the standards.

8.2 True color - Remove turbidity by centrifuging the sample until the supernatant is clear. The time required will depend upon the nature of the sample, the speed of the motor, and the radius of the centrifuge, but rarely will more than one hour be necessary. Compare the centrifuged sample with distilled water to insure that turbidity has been removed. If the sample is clear, then compare with standards as given in 8.1.

9. Calculation

9.1 Calculate the color units by means of the following equation:

$$\text{Color units} = \frac{A \times 50}{V}$$

Where: A = estimated color of diluted sample.

V = ml sample taken for dilution.

9.2 Report the results in whole numbers as follows:

Color Units	Record to Nearest
1-50	1
51-100	5
101-250	10
251-500	20

10. Precision and Accuracy

10.1 Precision and accuracy data are not available at this time.

Reference - Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 160, Method 118 (1971).

CYANIDE

1. Scope and Application

   1.1 This method is applicable to the determination of cyanide in surface waters, domestic and industrial wastes, and saline waters.

   1.2 The titration procedure using silver nitrate with p-dimethylaminobenzalrhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/l (0.2 mg/200 ml of absorbing liquid).

   1.3 The colorimetric procedure is used for concentrations below 1 mg/l of cyanide and is sensitive to about 5 μg/l.

2. Summary of Method

   2.1 The cyanide as hydrocyanic acid (HCN) is released from metallic cyanide complex ions by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

   2.2 The colorimetric measurement employs the pyridine-pyrazolone reaction in which the cyanide is coupled with free chlorine to form cyanogen chloride and then with pyridine to a glutaconic aldehyde. The aldehyde then reacts with 1-phenyl-3-methyl-5-pyrazolone to form a highly colored blue dye.

   2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

   3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium and mercuric ions.

4. Sampling Handling and Preservation

4.1 The sample should be collected in plastic bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.

4.2 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH of 11) at the time of collection.

4.3 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillate obtained with the preliminary screening procedure.

5.2 Sulfides are an interference that should be removed prior to distillation. Remove sulfides with pH adjustment to >11, addition of lead carbonate and mixing. Filter sample to remove lead sulfide. Repeat until no more lead sulfide is formed as evidenced by whiteness of the lead carbonate.

5.3 Oxidizing substances interfere and should be treated with ascorbic acid.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 ml (for titration).

6.3 Spectrophotometer suitable for measurements at 620 nm with a 1.0 cm cell or larger.

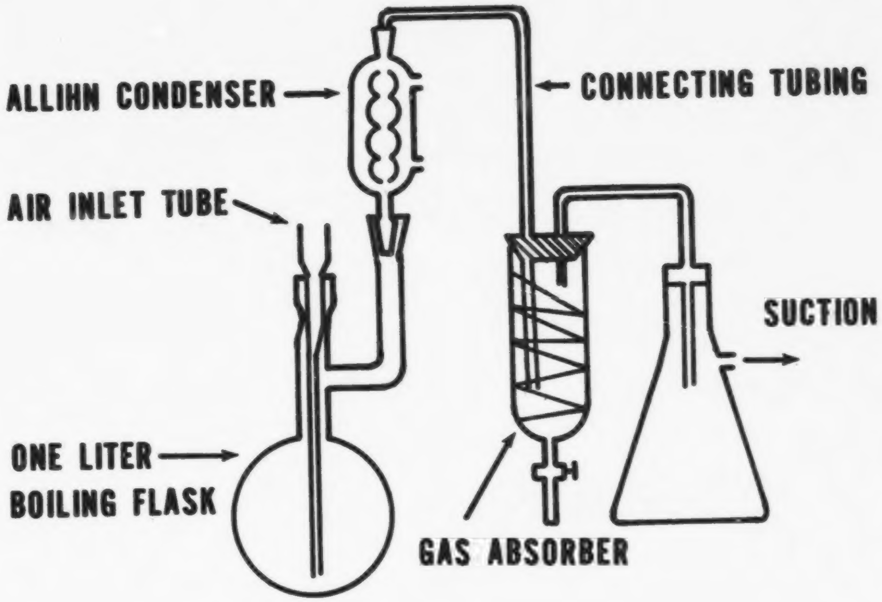
ALLIHN CONDENSER
CONNECTING TUBING
AIR INLET TUBE
SUCTION
ONE LITER BOILING FLASK
GAS ABSORBER

FIGURE 1

CYANIDE DISTILLATION APPARATUS

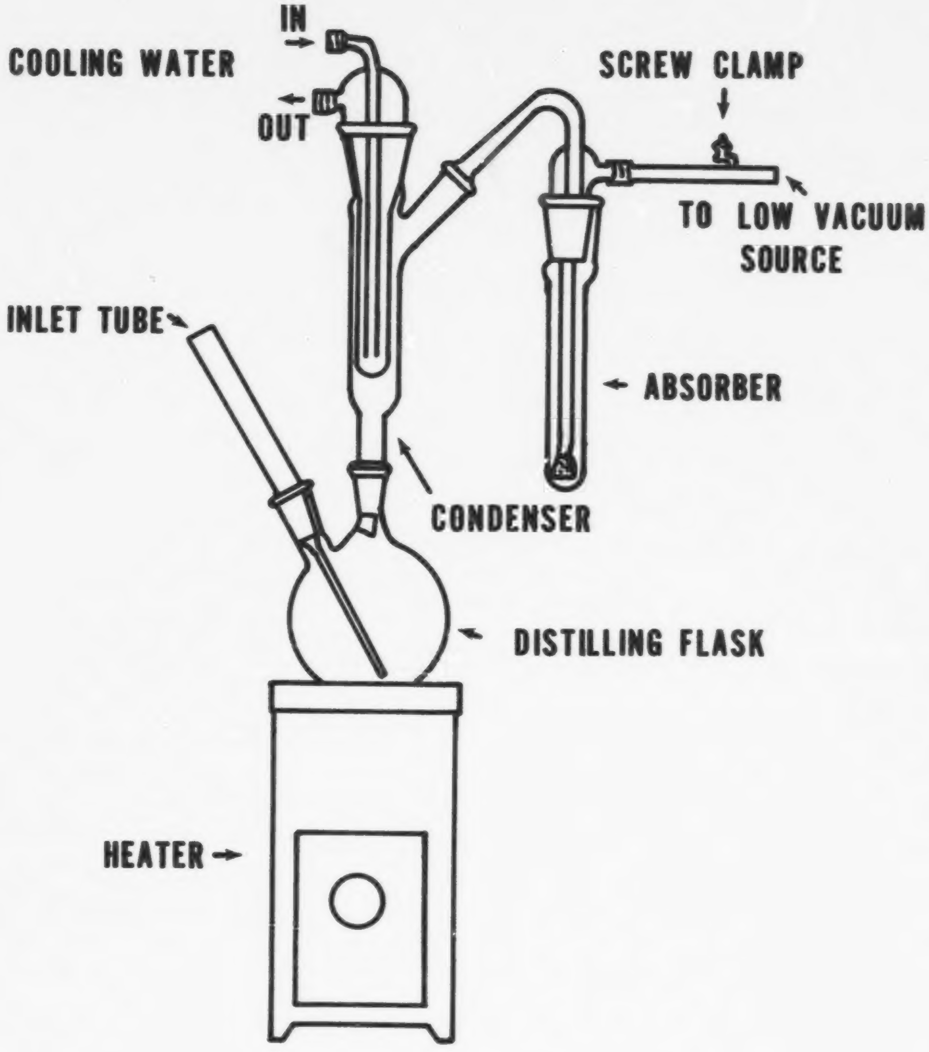
IN
COOLING WATER
OUT
SCREW CLAMP
TO LOW VACUUM SOURCE
INLET TUBE
ABSORBER
CONDENSER
DISTILLING FLASK
HEATER

FIGURE 2

CYANIDE DISTILLATION APPARATUS

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7. Reagents

7.1 Sodium hydroxide solution, 1 N. Dissolve 40 g of NaOH in distilled water, and dilute to a liter with distilled water.

7.2 Lead carbonate.

7.3 Ascorbic acid.

7.4 Mercuric chloride solution. Dissolve 34 g $HgCl_2$ in 500 ml distilled water.

7.5 Magnesium chloride solution. Dissolve 51 g $MgCl_2.6H_2O$ in 100 ml distilled water.

7.6 Sulfuric acid, concentrated.

7.7 Sodium dihydrogenphosphate, 1 M. Dissolve 138 g of $NaH_2PO_4.H_2O$ in one liter of distilled water. Refrigerate this solution.

7.8 Stock cyanide solution. Dissolve 2.51 g of KCN and 2 g KOH in one liter of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 ml = 1 mg CN^-.

7.9 Standard cyanide solution, intermediate. Dilute 10 ml of stock (1 ml = 1 mg CN) to a liter of distilled water (1 ml = 10 µg).

7.10 Standard cyanide solution. Prepare fresh daily by diluting 100 ml of intermediate cyanide solution to a liter of distilled water and store in a glass stoppered bottle. One ml = 1.0 µg CN (1.0 mg/l).

7.11 Standard silver nitrate solution, 0.0192 N. Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in water, and dilute to 1.0 liter (1 ml = 1 mg CN).

Preceding pa[illegible] blank

7.12 Rhodanine indicator. Dissolve 20 mg of p-dimethylamino-benzalrhodanine in 100 ml of acetone.

7.13 Chloramine T solution. Dissolve 1.0 g of white water soluble Chloramine T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.14 Pyridine-pyrazolone solution.

7.14.1 One-phenyl-3-methyl-5-pyrazolone reagent. Weigh 0.25 g of 3-methyl-1-phenyl-2-pyrazolone-5-one and dissolve in 50 ml of distilled water by heating to 60°C. Cool after reagent is in solution.

7.14.2 Three, 3'Dimethyl-1,1'-diphenyl-4,4'-bi-2 pyrazolone - 5,5' dione (bispyrazolone). Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.14.3 Pour solution 7.14.1 through nonacid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution 7.14.2 collecting the filtrate in the same container as filtrate from 7.14.1. Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

8. Procedure

8.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1-liter boiling flask. Add 50 ml of 1 N sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

8.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately 1 bubble of air per second enters the boiling flask through the air inlet tube. (Caution: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube).

8.3 Add 10 ml of mercuric chloride solution (7.4) and 40 ml of magnesium chloride solution (7.5) through the air inlet tube. Rinse the air inlet tube with a few ml of distilled water and allow the air flow to mix the contents of the flask for at least 3 minutes.

8.4 Slowly add 25 ml of concentrated sulfuric acid (7.6) through the air inlet tube and rinse with distilled water.

8.5 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling of the boiling flask disconnect absorber and close off the vacuum source.

8.6 Drain the solution from the absorber into a 250 ml volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.7 Withdraw 50 ml of the solution from the volumetric flask and transfer to a 100-ml volumetric flask. Add 10 ml of sodium phosphate solution (7.7) and 0.2 ml of Chloramine T solution (7.13) and mix. Add an additional 5 ml of the sodium phosphate (7.7), followed by 5 ml of mixed pyridine-pyrazolone solution, (7.14.3), bring to mark with distilled water and mix. Allow 40 minutes for color development.

8.8 Read absorbance at 620 nm using at least a 1.0 cm cell.

8.9 Prepare a series of standards by diluting suitable volumes of standard solution to 500.0 ml with distilled water as follows:

ml of Standard Solution (1.0 ml = 1 µg CN)	Conc., When Diluted to 500 ml, mg/1 CN
0 (Blank)	0
5.0	0.01
10.0	0.02
20.0	0.04
50.0	0.10
100.0	0.20
150.0	0.30
200.0	0.40

8.9.1 Standards must be treated in the same manner as the samples, as outlined in 8.1 through 8.8 above.

8.9.2 Prepare a standard curve by plotting absorbance of standards vs. cyanide concentrations.

8.9.3 Subsequently, at least two standards (a high and a low) should be treated as in 8.9.1 to verify standard curve. If results are not comparable (±20%), a complete new standard curve must be prepared.

8.9.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.9) or the working standard (7.10) to insure a level of 10 µg/l or a significant increase in absorbance value. Proceed with the analysis as in Procedure (8.) using the same flask and system from which the previous sample was just distilled.

8.10 Alternatively, if the sample contains more than 1 mg of CN^- transfer the distillate, or a suitable aliquot diluted to 250 ml, to a 500-ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.11 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the amount of sodium hydroxide and indicator as the sample.

8.12 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 ml microburet may be conveniently used to obtain a more precise titration.

9. Calculation

9.1 Using the titrimetric procedure, calculate concentration of CN, mg/l, directly from prepared standard curve.

9.2 Using the colorimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(A-B) \times 1000}{\text{Vol. of original sample}} \times \frac{250}{\text{Vol. of aliquot titrated}}$$

where:

A = volume of $AgNO_3$ for titration of sample.

B = volume of $AgNO_3$ for titration of blank.

10. Precision and Accuracy

10.1 A synthetic sample prepared by the Analytical Reference Service (PHS) at a known concentration of 0.02 mg/l CN was analyzed by 47 analysts; the data showed a standard deviation of 0.035 mg/l for the titrimetric procedure and 0.020 mg/l for the colorimetric procedure. Similarly, at a concentration of 1.10 mg/l of CN, the data showed a standard deviation of 0.333 mg/l for the titrimetric procedure and 0.306 mg/l for the colorimetric procedure.

References

1. Bark, L. S., and Higson, H. G. Investigation of reagents for the colorimetric determination of small amounts of cyanide. Talanta, 2:471-479 (1964).
2. Elly, C. T. Recovery of cyanides by modified Serfass distillution. Journal Water Pollution Control Federation, 40:848-856 (1968).

DISSOLVED OXYGEN

(Modified Winkler With Full-Bottle Technique)

STORET NO. 00300

1. Scope and Application

1.1 This method is applicable for use with most wastewaters and streams that contain nitrate nitrogen and not more than 1 mg/l of ferrous iron. Other reducing or oxidizing materials should be absent. If 1 ml fluoride solution is added before acidifying the sample and there is no delay in titration, the method is also applicable in the presence of 100-200 mg/l ferric iron.

1.2 The Dissolved Oxygen Probe technique (see p 60) gives comparable results on all sample types.

1.3 The azide modification is not applicable under the following conditions: (a) samples containing sulfite, thiosulfate, polythionate, appreciable quantities of free chlorine or hypochlorite; (b) samples high in suspended solids; (c) samples containing organic substances which are readily oxidized in a highly alkaline solution, or which are oxidized by free iodine in an acid solution; (d) domestic sewage; (e) biological flocs; and (f) where sample color interferes with endpoint detection. In instances where the azide modification is not applicable, the DO probe should be used.

2. Summary of Method

2.1 The sample is treated with manganous sulfate, potassium hydroxide, and potassium iodide (the latter two reagents combined in one solution) and finally sulfuric acid. The initial precipitate of manganous hydroxide, $Mn(OH)_2$, combines with the dissolved oxygen in the sample to form a brown precipitate, manganic hydroxide, $Mn\,O(OH)_2$. Upon acidification, the manganic hydroxide forms manganic sulfate which acts as an oxidizing agent to release free iodine from the potassium iodine. The iodine, which is stoichiometrically equivalent to the dissolved oxygen in the sample is then titrated with sodium thiosulfate.

3. Interferences

3.1 There are a number of interferences to the dissolved oxygen test, including oxidizing and reducing agents, nitrate ion, ferrous iron, and organic matter.

3.2 Various modifications of the original Winkler procedure for dissolved oxygen have been developed to compensate or eliminate interferences. The Alsterberg modification is commonly used to successfully eliminate the nitrite interference, the Rideal-Stewart modification is designed to eliminate ferrous iron interference, and the Theriault procedure is used to compensate for high concentration of organic materials.

3.3 Most of the common interferences in the Winkler procedure may be overcome by use of the dissolved oxygen probe.

4. Sample Handling and Preservation

4.1 Where possible, collect the sample in a 300 ml BOD incubation bottle. Special precautions are required to avoid entrainment or solution of atmospheric oxygen or dissolution of dissolved oxygen.

4.2 Where samples are collected from shallow depths (less than 5 feet), use of an APHA-type sampler is recommended. Use of a Kemmerer type sampler is recommended for samples collected from depths of greater than 5 feet.

4.3 When a Kemmerer sampler is used, the BOD sample bottle should be filled to overflowing. (Overflow for approximately 10 seconds). Outlet tube of Kemmerer should be inserted to bottom of BOD bottle. Care must be taken to prevent turbulence and the formation of bubbles when filling bottle.

4.4 The sample temperature should be recorded at time of sampling as precisely as required.

4.5 Do not delay the determination of dissolved oxygen in samples having an appreciable iodine demand or containing ferrous iron. If samples must be preserved either method 4.5.1 or 4.5.2, below, may be employed.

4.5.1 Add 2 ml of manganous sulfate reagent and then 2 ml of alkali azide reagent to the sample contained in the BOD bottle. Both reagents must be added well below the surface of the liquid. Stopper the bottle immediately and mix the contents thoroughly. The sample should be stored at the temperature of the collection water, or water sealed and kept at a temperature of 10 to 20°C, in the dark.

4.5.2 Add 0.7 ml of concentrated H_2SO_4 and 1 ml sodium azide solution (2 g NaN_3 in 100 ml distilled water) to the sample in the DO bottle. Store sample as in 4.5.1. Complete the procedure using 2 ml of manganous sulfate solution, 3 ml alkali iodide solution, and 2 ml of concentrated H_2SO_4.

4.6 If either preservation technique is employed, complete the analysis within 4-8 hours after sampling.

5. Apparatus

5.1 Sample bottles - 300 ml ±3 ml capacity BOD incubation bottles with tapered ground glass pointed stoppers and flared mouths.

5.2 Pipets - with elongated tips capable of delivering 2.0 ml ±0.1 ml of reagent.

6. Reagents

6.1 Manganous sulfate solution: Dissolve 480 g manganous sulfate ($MnSO_4 \cdot 4H_2O$) in distilled water and dilute to 1 liter.

6.1.1 Alternately, use 400 g of $MnSO_4.2H_2O$ or 364 g of $MnSO_4.H_2O$ per liter. When uncertainty exists regarding the water of crystallization, a solution of equivalent strength may be obtained by adjusting the specific gravity of the solution to 1.270 at 20°C.

6.2 Alkaline iodide solution: Dissolve 500 g of sodium hydroxide (NaOH) or 700 g of potassium hydroxide (KOH) and 135 g of sodium iodide (NaI) or 150 g of potassium iodide (KI) in distilled water and dilute to 1 liter. To this solution add 10 g of sodium azide (NaN_3) dissolved in 40 ml of distilled water.

6.3 Sulfuric acid, concentrated.

6.4 Starch solution: Prepare an emulsion of 10 g soluble starch in a mortar or beaker with a small quantity of distilled water. Pour this emulsion into 1 liter of boiling water, allow to boil a few minutes, and let settle overnight. Use the clear supernate. This solution may be preserved by the addition of 5 ml per liter of chloroform and storage in a 10°C refrigerator.

6.4.1 Dry, powdered starch indicators such as "thyodene" may be used in place of starch solution.

6.5 Potassium fluoride solution: Dissolve 40 g $KF.2H_2O$ in distilled water and dilute to 100 ml.

6.6 Sodium thiosulfate, stock solution, 0.75 N: Dissolve 186.15 g $Na_2S_2O_3.5H_2O$ in boiled and cooled distilled water and dilute to liter. Preserve by adding 5 ml chloroform.

6.7 Sodium thiosulfate standard titrant, 0.0375 N: Prepare by diluting 50.0 ml of stock solution to 1 liter. Preserve by adding 5 ml of chloroform. Standard sodium thiosulfate, exactly 0.0375 N is equivalent to 0.300 mg of DO per 1.00 ml. Standardize with 0.0375 N potassium biiodate.

6.8 Potassium biiodate standard, 0.0375 N: Dissolve 4.873 g potassium biiodate, previously dried 2 hours at 103°C, in 1.0 liter of distilled water. Dilute 250 ml to 1.0 liter for 0.0375 N biiodate solution.

6.9 Standardization of 0.0375 N sodium thiosulfate: Dissolve approximately 2 g (±1.0 g) KI in 100 to 150 ml distilled water; add 10 ml of 10% H_2SO_4 followed by 20 ml standard potassium biiodate. Place in dark for 5 minutes, dilute to 300 ml, and titrate with the standard sodium thiosulfate to a pale straw color. Add 1-2 ml starch solution and continue the titration drop by drop until the blue color disappears. Run in duplicate. Duplicate determinations should agree within ±0.05 ml.

7. Procedure

7.1 To the sample collected in the BOD incubation bottle, add 2 ml of the manganous sulfate solution followed by 2 ml of the alkali-iodide-azide reagent, well below the surface of the liquid; stopper with care to exclude air bubbles, and mix well by inverting the bottle several times. When the precipitate settles, leaving a clear supernatant above the manganese hydroxide floc, shake again. When settling has produced at least 100 ml of clear supernate, carefully remove the stopper and immediately add 2.0 ml of conc. H_2SO_4 (sulfamic acid packets, 3 g may be substituted for H_2SO_4)(1)

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(1) Kroner, R. C., Longbottom, J. E., Gorman, R., A Comparison of Various Reagents Proposed for Use in the Winkler Procedure for Dissolved Oxygen, PHS Water Pollution Surveillance System Applications and Development Report #12, Water Quality Section, Basic Data Branch, July 1964.

by allowing the acid to run down the neck of the bottle, re-stopper, and mix by gentle inversion until the iodine is uniformly distributed throughout the bottle. Complete the analysis within 45 minutes.

7.2 Transfer the entire bottle contents by inversion into a 500-ml wide mouth Erlenmeyer flask and titrate with 0.0375 N thiosulfate solution (where problems of stability arise, 0.0375 N phenylarsine oxide (PAO) may be substituted as titrant)(1) to a pale straw color. Add 1-2 ml of starch solution or 0.1 g of powdered indicator and continue to titrate to the first disappearance of the blue color.

7.3 If ferric iron is present (100 to 200 ppm), add 1.0 ml of KF solution before acidification.

7.4 Occasionally, a dark brown or black precipitate persists in the bottle after acidification. This precipitate will dissolve if the solution is kept for a few minutes longer than usual or, if particularly persistent, a few more drops of H_2SO_4 will effect dissolution.

8. Calculation

8.1 Each ml of 0.0375 sodium thiosulfate titrant is equivalent to 1 mg DO when the entire bottle contents are titrated.

8.2 If the results are desired in milliliters of oxygen gas per liter at 0°C and 760 mm pressure, multiply mg/1 DO by 0.698.

8.3 To express the results as percent saturation at 760 mm atmospheric pressure, the solubility data in Table 218 (Whipple & Whipple Table, p. 480, Standard Methods, 13th Edition) may be used. Equations for correcting the solubilities to barometric pressures other than mean sea level are given below the table.

8.4 The solubility of DO in distilled water at any barometric pressure, p (mm Hg), temperature, T°C, and saturated vapor pressure, μ (mm Hg), for the given T, may be calculated between the temperature of 0° and 30°C by:

$$\text{ml/l DO} = \frac{(P - \mu) \times 0.678}{35 + T}$$

and between 30° and 50°C by:

$$\text{ml/l DO} = \frac{(P - \mu) \times 0.827}{49 + T}$$

9. Precision and Accuracy

9.1 Exact data are unavailable on the precision and accuracy of this technique; however, reproducibility is approximately 0.2 ppm of DO at the 7.5 ppm level due to equipment tolerances and uncompensated displacement errors.

DISSOLVED OXYGEN

(Probe Method)

STORET NO. 00300

1. Scope and Application

   1.1 The probe method for dissolved oxygen is recommended for those samples containing materials which interfere with the modified Winkler procedure such as sulfite, thiosulfate, polythionate, mercaptans, free chlorine or hypochlorite, organic substances readily hydrolyzed in alkaline solutions, free iodine, intense color or turbidity, biological flocs, etc.

   1.2 The probe method is recommended as a substitute for the modified Winkler procedure in monitoring of streams, lakes, outfalls, etc., where it is desired to obtain a continuous record of the dissolved oxygen content of the water under observation.

   1.3 The probe method may be used as a substitute for the modified Winkler procedure in BOD determinations where it is desired to perform non-destructive DO measurements on a sample.

   1.4 The probe method may be used under any circumstances as a substitute for the modified Winkler procedure provided that the probe itself is standardized against the Winkler method on samples free of interfering materials.

   1.5 The electronic readout meter for the output from dissolved oxygen probes is normally calibrated in convenient scale (0 to 10, 0 to 15, 0 to 20 mg/l for example) with a sensitivity of approximately 0.05 mg/liter.

2. Summary of Method

   2.1 The most common instrumental probes for determination of dissolved oxygen in water are dependent upon electrochemical reactions. Under steady-state conditions, the current or potential can be correlated with DO concentrations. Interfacial dynamics at the probe-sample interface are a factor in probe response and a significant degree of interfacial turbulence is necessary. For precision performance, turbulence should be constant.

3. Sample Handling and Preservation

3.1 See 4.1, 4.2, 4.3, 4.4 under Modified Winkler Method.

4. Interferences

4.1 Dissolved organic materials are not known to interfere in the output from dissolved oxygen probes.

4.2 Dissolved inorganic salts are a factor in the performance of dissolved oxygen probe.

4.2.1 Probes with membranes respond to partial pressure of oxygen which in turn is a function of dissolved inorganic salts. Conversion factors for seawater and brackish waters may be calculated from dissolved oxygen saturation versus salinity data. Converson factors for specific inorganic salts may be developed experimentally. Broad variations in the kinds and concentrations of salts in samples can make the use of a membrane probe difficult.

4.2.2 The thallium probe requires the presence of salts in concentrations which provide a minimum conductivity of approximately 200 micromhos.

4.3 Reactive compounds can interfere with the output or the performance of dissolved oxygen probes.

4.3.1 Reactive gases which pass through the membrane of membrane probes may interfere. For example, chlorine will depolarize the cathode and cause a high probe-output. Long-term exposures to chlorine will coat the anode with the chloride of the anode metal and eventually desensitize the probe. Alkaline samples in which free chlorine does not exist will not interfere. Hydrogen sulfide will interfere with membrane probes if the applied potential is greater than the half-wave potential of the sulfide ion. If the applied potential is less than the half-wave potential, an interfering reaction will not occur, but coating of the anode with the sulfide of the anode metal can take place.

4.3.2 Sulfur compounds (hydrogen sulfide, sulfur dioxide and mercaptans, for example) cause interfering outputs from the thallium probe. Halogens do not interfere with the thallium probe.

4.4 At low dissolved oxygen concentrations, pH variation below pH 5 and above pH 9 interfere with the performance of the thallium probe (approximately ±0.05 mg/1 DO per pH unit). The performance of membrane probes is not affected by pH changes.

4.5 Dissolved oxygen probes are temperature sensitive, and temperature compensation is normally provided by the manufacturer. The thallium probe has a temperature coefficient of 1.9 m/°C. Membrane probes have a temperature coefficient of 4 to 6 percent/°C dependent upon the membrane employed.

5. Apparatus

5.1 No specific probe or accessory is especially recommended as superior. However, probes which have been evaluated or are in use and found to be reliable are the Weston & Stack DO Analyzer Model 30 and the Yellow Springs Instrument (YSI) Model 54.

6. Calibration

Follow manufacturer instructions.

7. Procedure

Follow manufacturer instructions.

8. Calculation

Follow manufacturer instructions.

9. Precision and Accuracy

Manufacturer's specification claim 0.1 mg/l repeatability with ±1% accuracy.

FLUORIDE

(SPADNS Method with Bellack Distillation)

STORET NO. 00950

1. Scope and Application

   1.1 This method is applicable to the measurement of fluoride in drinking waters, surface waters, domestic wastes and industrial wastes and saline waters. It is the method to be used when the accessories for the probe method are not available.

   1.2 The method covers the range from 0.1 to about 2.5 mg/l F.

2. Summary of Method

   2.1 Following distillation to remove interferences the sample is treated with the SPADNS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl-SPADNS dye is a function of the fluoride concentration.

3. Comments

   3.1 The SPADNS reagent is more tolerant of interfering materials than other accepted fluoride reagents. Reference to Table 121, (1) page 169, Standard Method for the Examination of Waters and Wastewaters, 13th Edition, will help the analyst decide if distillation is required. The addition of the highly colored SPADNS reagent must be done with utmost accuracy because the fluoride concentration is measured as a difference of absorbance in the blank and the sample. A small error in reagent addition is the most prominent source of error in this test.

4. Precision and Accuracy

   4.1 On a sample containing 0.83 mg/l F with no interferences, 53 analysts using the Bellack distillation and the SPADNS reagent obtained a mean of 0.81 mg/l F with a standard deviation of 0.089 mg/l.

4.2 On a sample containing 0.57 mg/1 F (with 200 mg/1 SO_4 and 10 mg/1 Al as interferences) 53 analysts using the Bellack distillation obtained a mean of 0.60 mg F/1 with a standard deviation of 0.103 mg/1.

4.3 On a sample containing 0.68 mg/1 F (with 200 mg/1 SO_4, 2 mg/1 Al and 2.5 mg/1 $[NaPO_3]_6$ as interferences), 53 analysts using the Bellack distillation obtained a mean of 0.72 mg/1 F with a standard deviation of 0.092 mg/1.

4.4 Analytical Reference Service, Sample 111-B water, Fluoride, August, 1961.

5. Reference

The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewaters, pp 171-172 (Method No. 121A, Preliminary Distillation Step) and pp 174-176 (Method 121C, SPADNS) 13th Edition, (1971).

American Society for Testing and Materials, Part 23, pp 213-218, Method No. D1179-68, (1970).

FLUORIDE

(Automated Complexone Method)

STORET NO. 00950

1. Scope and Application

   1.1 This method is applicable to surface waters, domestic and industrial wastes, and saline waters. The applicable range of the method is 0.05 to 1.5 mg F/1. Twelve samples per hour can be analyzed.

2. Summary of Method

   2.1 Fluoride ion reacts with the red cerous chelate of alizarin complexone. It is unlike other fluoride procedures in that a positive color is developed as contrasted to a bleaching action in previous methods.

3. Sample Handling and Preservation

   3.1 No special requirements.

4. Interferences

   4.1 Method is free from most anionic and cationic interferences, except aluminum, which forms an extremely stable fluoro compound, AlF_6^{-3}. This is overcome by treatment with 8-hydroxyquinoline to complex the aluminum and by subsequent extraction with chloroform.

5. Apparatus

   5.1 Technicon AutoAnalyzer Unit consisting of:

      5.1.1 Sampler I.

      5.1.2 Manifold.

      5.1.3 Proportioning pump.

      5.1.4 Continuous filter.

      5.1.5 Colorimeter equipped with 15 mm tabular flow cell and 650 nm filters.

      5.1.6 Recorder equipped with range expander.

6. Reagents

6.1 Sodium acetate solution: Dissolve 272 g (2 moles) of sodium acetate in distilled water and dilute to 1 liter.

6.2 Acetic acid-8-hydroxyquinoline solution: Dissolve 6 g of 8-hydroxyquinoline in 34 ml of conc. acetic acid, and dilute to 1 liter.

6.3 Chloroform: Analytical reagent grade.

6.4 Ammonium acetate solution (6.7%): Dissolve 67 g of ammonium acetate in distilled water and dilute to 1 liter.

6.5 Hydrochloric acid (2 N): Dilute 172 ml of conc. HCl to 1 liter.

6.6 Lanthanum alizarin fluoride blue solution*: Dissolve 0.18 g of alizarin fluoride blue in a solution containing 0.5 ml of conc. ammonium hydroxide and 15 ml of 6.7% ammonium acetate. Add a solution that contains 41 g of anhydrous sodium carbonate and 70 ml of glacial acetic acid in 300 ml of distilled water. Add 250 ml of acetone. Dissolve 0.2 g of lanthanum oxide in 12.5 ml of 2 N hydrochloric acid and mix with above solution. Dilute to 1 liter.

6.7 Stock Solution: Dissolve 2.210 g of sodium fluoride in 100 ml of distilled water and dilute to 1 liter. 1 ml = 1.0 mg F.

6.8 Standard Solution: Dilute 10.0 ml of stock solution to 1 liter. 1 ml = 0.01 mg F.

6.8.1 Using standard solution, prepare the following standards in 100-ml volumetric flasks:

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*J. T. Baker Laboratory Chemical No. J112 or equivalent.

mg F/1	ml Standard Solution/100 ml
0.05	0.5
0.10	1.0
0.20	2.0
0.40	4.0
0.60	6.0
0.80	8.0
1.00	10.0
1.20	12.0
1.50	15.0

7. Procedure

7.1 Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.

7.4 Arrange fluoride standards in Sampler in order of decreasing concentration. Complete loading of Sampler tray with unknown samples.

7.5 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed fluoride standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

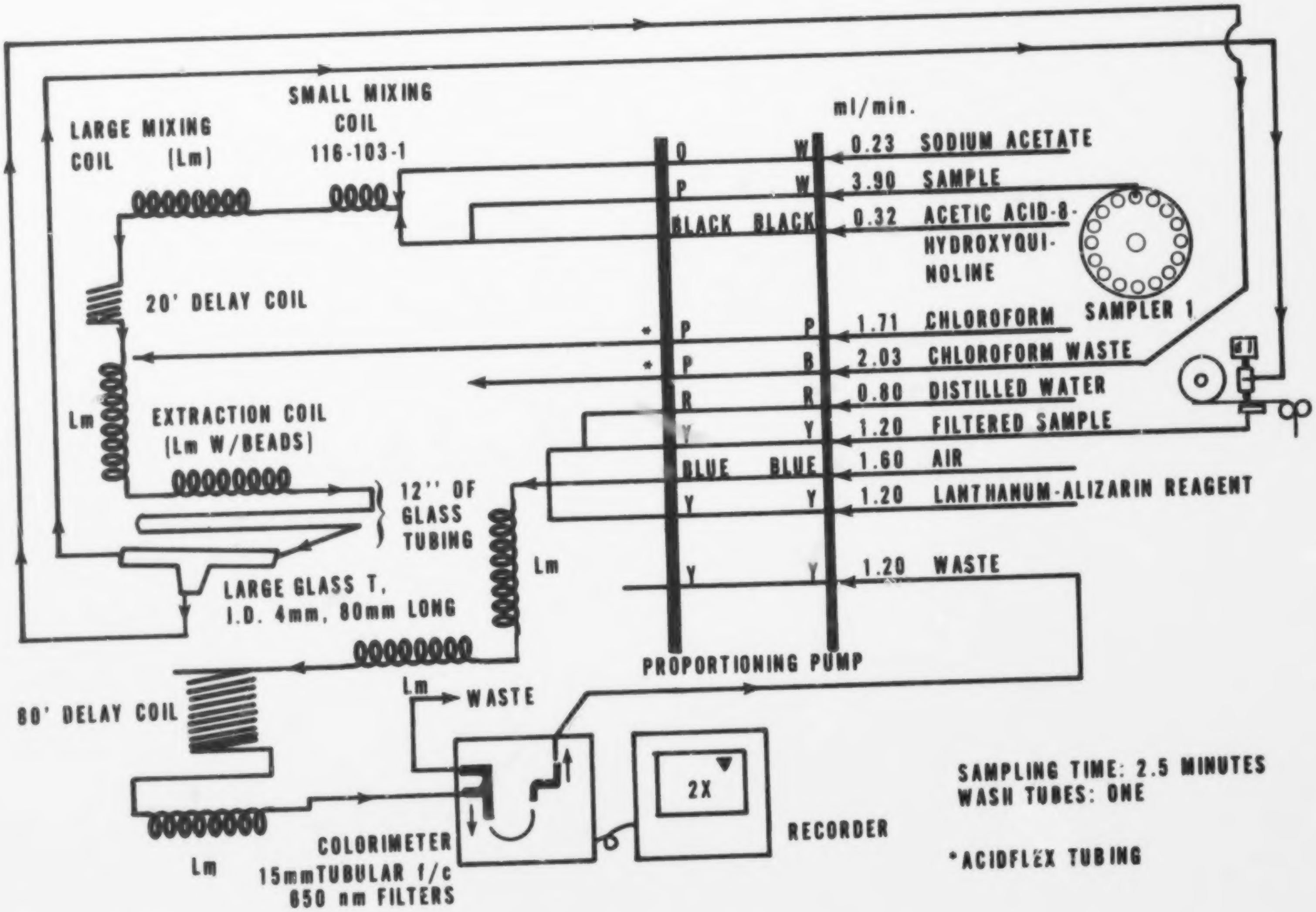
9. Precision and Accuracy

9.1 In a single laboratory, using surface water samples at concentrations of 0.06, 0.15, 0.55, and 1.08 mg F/1, the standard deviation was ±0.018 (AQC Laboratory).

9.2 In a single laboratory, using surface water samples at concentrations of 0.14 and 1.25 mg F/l recoveries were 89% and 102%, respectively (AQC Laboratory):

References

1. R. Greenhaigh and J. P. Riley, "The Determination of Fluorides in Natural Waters, with Particular Reference to Sea Water." Anal. Chim. Acta, 25, 179 (1961).
2. K. M. Chan and J. P. Riley, "The Automatic Determination of Fluoride in Sea Water and Other Natural Waters." Anal. Chim. Acta, 35, 365 (1966).


LARGE MIXING COIL (Lm)
SMALL MIXING COIL 116-103-1
20' DELAY COIL
Lm
EXTRACTION COIL (Lm W/BEADS)
12'' OF GLASS TUBING
LARGE GLASS T, I.D. 4mm, 80mm LONG
Lm
80' DELAY COIL
Lm
WASTE
Lm
COLORIMETER 15mmTUBULAR f/c 650 nm FILTERS
2X
RECORDER
PROPORTIONING PUMP
ml/min.
O
W
0.23
SODIUM ACETATE
P
W
3.90
SAMPLE
BLACK
BLACK
0.32
ACETIC ACID-8-HYDROXYQUINOLINE
SAMPLER 1
*
P
P
1.71
CHLOROFORM
*
P
B
2.03
CHLOROFORM WASTE
R
R
0.80
DISTILLED WATER
Y
Y
1.20
FILTERED SAMPLE
BLUE
BLUE
1.60
AIR
Y
Y
1.20
LANTHANUM-ALIZARIN REAGENT
Y
Y
1.20
WASTE

SAMPLING TIME: 2.5 MINUTES
WASH TUBES: ONE

*ACIDFLEX TUBING

FIGURE 1. FLUORIDE MANIFOLD

FLUORIDE

(Specific Ion Electrode Method)

STORET NO. 00950

1. Scope and Application

1.1 This method is applicable to the measurement of fluoride in finished waters, natural waters, brines, and industrial waste waters and the need for distillation of the sample is eliminated.

1.2 Concentrations of fluoride from 0.1 up to 1000 mg/liter may be measured.

2. Summary of Method

2.1 The fluoride is determined potentiometrically using a specific ion fluroide electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a specific ion meter having a direct concentration scale for fluoride.

2.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/Ag Cl, Cl^- (0.3), F^- (0.001) LaF_3/ test solution/SCE/.

3. Interferences

3.1 Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of Si^{+4}, Fe^{+3} and Al^{+3} interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer (described below) containing a strong, chelating agent preferentially complexes aluminum (the most common interference), silicon, and iron, and eliminates the pH problem.

4. Sampling Handling and Preservation

4.1 No special requirements.

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5. Apparatus

   5.1 Electrometer, (pH meter) with expanded mv scale or a specific ion meter such as the Orion 400 Series.

   5.2 Fluoride Ion Activity Electrode, such as Orion No. 94-09(1).

   5.3 Reference electrode, single junction, sleeve-type, such as Orion No. 90-01, Beckman No. 40454, or Corning No. 476010.

   5.4 Magnetic Mixer, Teflon-coated stirring bar.

6. Reagents

   6.1 Buffer solution, pH 5.0-5.5. To approximately 500 ml of distilled water in a one-liter beaker add 57 ml of glacial acetic acid, 58 g of sodium chloride and 2 g of CDTA(2). Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer solution to a one-liter volumetric flask and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.

   Note - CDTA replaces citric acid used in the original buffer formula. It is a strong chelating agent and more effectively ties up aluminum than the original citric acid.

   6.2 Sodium fluoride, stock solution (1.0 mg = 0.01 mg F). Dissolve 0.2210 g of sodium fluoride in water and dilute to 1.0 liter. Dilute 100 ml of this solution to 1.0 liter with water. Store in chemical-resistant glass or polyethylene.

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(1) Patent No. 3,431,182 (March 4, 1969).

(2) CDTA is the abbreviated designation of 1,2-cyclohexylene dinitrilo tetraacetic acid, (Mathieson, Coleman & Bell, Cat. No. P8661) or cyclohexane diamine tetraacetic acid (Merck-Titriplex IV or Baker Cat. No. G083).

7. Calibration

7.1 Prepare a series of standards using the fluoride stock solution (1 ml = 0.01 mg F) in the range of 0 to 2.00 mg/liter by diluting appropriate volumes to 50 ml. The following series may be used:

Milliliters of Stock (1.0 ml = 0.01 mg/F)	Concentration when Diluted to 50 ml, mg F/liter
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
8.00	1.60
10.00	2.00

7.2 Calibration of Electrometer: Immerse the electrodes in each stock solution starting with the lowest concentration and measure the developed potential while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. Using semilogarithmic graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.3 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

8. Procedure

8.1 Place 50.0 ml of sample and 50.0 ml of buffer in a 150-ml beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/liter F, it may require as long as five minutes to reach a stable meter reading; higher concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve. If a specific ion meter is used, read the fluoride level in the unknown sample directly in mg/l on the fluoride scale.

9. Precision and Accuracy

9.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 0.85 mg/l fluoride and no interferences was analyzed by 111 different analysts; a mean of 0.84 mg/l with a standard deviation of ±0.030 was obtained.

9.2 On the same study, a synthetic sample containing 0.75 mg/l fluoride, 2.5 mg/l polyphosphate and 300 mg/l alkalinity, was analyzed by the same 111 analysts; a mean of 0.75 mg/l fluoride with a standard deviation of ±0.036 was obtained.

HARDNESS

STORET Number: 00900

1. Scope and Application

   1.1 This method is applicable to drinking waters and surface waters, domestic and industrial wastes.

   1.2 The method is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25 mg $CaCO_3$ per 50 ml sample.

   1.3 Automated titration may be used.

2. Summary of Method

   2.1 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium dihydrogen ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction is detected by means of Chrome Black T or Calmagite,(1) which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

3. Comments

   3.1 Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide.

      3.1.1 Routine addition of sodium cyanide solution (CAUTION: Deadly poison) to prevent potential metallic interference is recommended.

4. Precision and Accuracy

   4.1 Forty-three analysts in nineteen laboratories analyzed six synthetic water samples containing exact increments of calcium and magnesium salts, with the following results:

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(1) Hach Cat. No. 825 or equivalent.

Increment as Total Hardness mg/liter as $CaCO_3$	Precision as Standard Deviation mg/liter as $CaCO_3$	Accuracy as	
		Bias, %	Bias, mg P/liter $CaCO_3$
31	2.87	-0.87	-0.003
33	2.52	-0.73	-0.24
182	4.87	-0.19	0.4
194	2.98	-1.04	-2.0
417	9.65	-3.35	-13.0
444	8.73	-3.23	-14.3

(FWPCA Method Study 1, Mineral and Physical Analyses)

4.2 In a single laboratory (AQC), using surface water samples at an average concentration of 194 mg $CaCO_3$/l, the standard deviation was ± 3.

5. Reference

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 179, Method 122B (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p. 187, Method D1126-67 (1970).

HARDNESS, TOTAL

(Automated Method)

STORET NO. 00900

1. Scope and Application

1.1 This automated method is applicable to surface and saline waters. The applicable range is 10 to 400 mg/l as $CaCO_3$. Approximately 12 samples per hour can be analyzed.

2. Summary of Method

2.1 The disodium magnesium EDTA exchanges magnesium on an equivalent basis for any calcium and/or other cations to form a more stable EDTA chelate than magnesium. The free magnesium reacts with calmagite at a pH of 10 to give a red-violet complex. Thus, by measuring only magnesium concentration in the final reaction stream, an accurate measurement of total hardness is possible.

3. Sample Handling and Preservation

3.1 No special requirements.

4. Interferences

4.1 No significant interferences.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I.

5.1.2 Continuous Filter.

5.1.3 Manifold.

5.1.4 Proportioning Pump.

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.

5.1.6 Recorder equipped with range expander.

6. Reagents

6.1 Buffer: Dissolve 67.6 g NH_4Cl in 572 ml of NH_4OH and dilute to 1 liter.

6.2 Calmagite(1): Dissolve 0.25 g in 500 ml of distilled water by stirring approximately 30 minutes on a magnetic stirrer. Filter.

6.3 Magnesium EDTA: Dissolve 0.2 g of MgEDTA in 1 liter of distilled water.

6.4 Stock Solution: Weigh 1.0 g of calcium carbonate (pre-dried at 105°C) into 500 ml Erlenmeyer flask; add 1:1 HCl until all $CaCO_3$ has dissolved. Add 200 ml of distilled water and boil for a few minutes. Cool, add a few drops of methyl red indicator, and adjust to the orange color with 3N NH_4OH and dilute to 1 liter. 1.0 ml = 1.0 mg $CaCO_3$.

6.4.1 Dilute each of the following volumes of stock solutions to 250 ml for appropriate standards:

Stock Solution, ml	$CaCO_3$, mg/l
2.5	10.0
5.0	20.0
10.0	40.0
15.0	60.0
25.0	100
35.0	140
50.0	200
75.0	300
100.0	400

7. Procedure

7.1 Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

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(1) Hach Cat. No. 825 or equivalent.

7.3 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.

7.4 Arrange working standards in Sampler in order of decreasing concentration. Complete loading of Sampler tray with unknown samples.

7.5 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

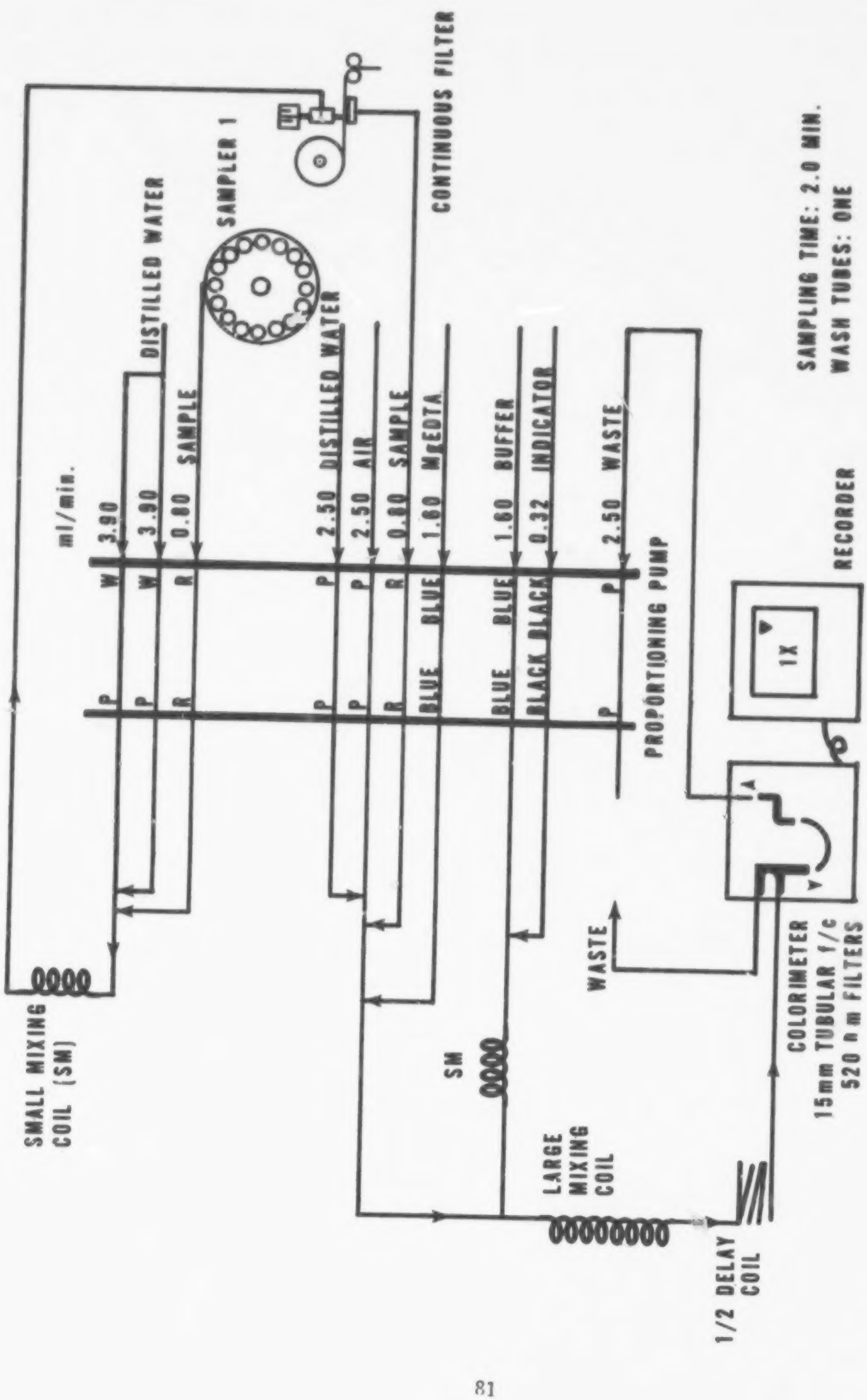
9.1 In a single laboratory (AQC), using surface water samples at concentrations of 19, 120, 385, and 366 mg/l as $CaCO_3$, the standard deviations were ±1.5, ±1.5, ±4.5, and ±5.0, respectively.

9.2 In a single laboratory (AQC), using surface water samples at concentrations of 39 and 296 mg/l as $CaCO_3$, recoveries were 89% and 93%, respectively.

References

1. Technicon AutoAnalyzer Methodology, Bulletin No. 2, Technicon Controls, Inc., Chauncey, New York (July 1960).

2. Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 179, Method 122B (1971).



CONTINUOUS FILTER
SAMPLER 1
DISTILLED WATER
ml/min.
3.90
3.90
0.80 SAMPLE
2.50 DISTILLED WATER
2.50 AIR
0.80 SAMPLE
1.60 MgEDTA
1.60 BUFFER
0.32 INDICATOR
2.50 WASTE
W W R P P R BLUE BLUE BLACK P
P P R P P R BLUE BLUE BLACK P
PROPORTIONING PUMP
RECORDER
1X
SMALL MIXING COIL (SM)
SM
LARGE MIXING COIL
1/2 DELAY COIL
WASTE
COLORIMETER
15mm TUBULAR f/c
520 nm FILTERS

SAMPLING TIME: 2.0 MIN.
WASH TUBES: ONE

FIGURE 1. HARDNESS MANIFOLD

METALS

(Atomic Absorption Methods)

1. Scope and Application

   1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in surface waters, domestic and industrial wastes, and saline waters.

   1.2 Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table 1, however, provide some indication of the concentration ranges measurable. In the majority of instances the concentration range shown in the table may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength. Detection limits may also be extended through concentration of the sample or through solvent extraction techniques. Table 1 lists detection limits, sensitivities, and the optimum concentration ranges achieved directly on the sample using the Instrumentation Laboratories, Model IL-153 without scale expansion (Pos 2.5). The boat technique developed at Perkin-Elmer for use with the PE303 or 403 may also be used to extend absolute detection limits.(1)

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TABLE 1

Concentration Ranges

Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l
Aluminum	0.1	0.4	10 - 1000
Arsenic	0.05	1.0	10 - 100
Cadmium	0.001	0.004	0.1 - 2
Calcium	0.003	0.07	1 - 200
Chromium	0.01	0.02	1 - 200
Copper	0.005	0.04	0.1 - 10
Iron	0.004	0.006	0.1 - 20
Lead	0.01	0.06	1 - 10
Magnesium	0.0005	0.005	0.01 - 2
Manganese	0.005	0.04	0.1 - 20
Potassium	0.005	0.01	0.01 - 2
Silver	0.01	0.05	0.1 - 20
Sodium	0.001	0.003	1 - 200
Zinc	0.005	0.02	0.1 - 2

2. Summary of Method

2.1 Atomic absorption spectroscopy is similar to flame emission photometry in that a sample is atomized and aspirated into a flame. Flame photometry, however, measures the amount of light emitted, whereas, in atomic absorption spectrophotometry a light beam is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. In many instances absorption is more sensitive because it depends upon the presence of free unexcited atoms and generally the ratio of unexcited to excited atoms at a given moment is very high. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.2 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy(2) the technique generally is limited to metals in solution or solubilized through some form of sample processing. Thus, it is a relatively simple matter to determine metals in the dissolved fraction by aspirating a filtered portion of the water sample.

2.2.1 In those instances where complete characterization of a sample is desired, the suspended material must also be analyzed. This may be accomplished by filtration and acid digestion of the suspended material. Metallic constituents in this acid digest are subsequently determined and the sum of the dissolved plus suspended concentrations will then provide the total concentrations present.

2.2.2 The sample may also be treated with acid before filtration to measure what may be termed "extractable" concentrations.

3. Definition of Terms

3.1 Sensitivity: is the concentration in milligrams of metal per liter that produces an absorption of 1%.

3.2 Detection Limit: is defined as the concentration that produces absorption equivalent to twice the magnitude of the fluctuation in the background (zero absorption).

3.3 Dissolved Metals: those constituents (metals) which will pass through a 0.45 μ membrane filter.

3.4 Suspended Metals: those constituents (metals) which are retained by a 0.45 μ membrane filter.

3.5 Total Metals: the concentration of metals determined on an unfiltered sample following vigorous digestion (Section 4.1.3), or the sum of the concentrations of metals in both the dissolved and suspended fractions.

3.6 Extractable Metals: the concentration of metals in an unfiltered sample following digestion with hot dilute mineral acid (Section 4.1.4).

4. Sample Handling and Preservation

4.1 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle should be thoroughly washed with detergent and tap water; rinsed with chromic acid, tap water, 1:1 nitric acid, tap water and finally distilled water in that order. Before collection of the sample a decision must be made as to the type of data desired, i.e., dissolved, suspended, total or extractable.

4.1.1 For the determination of dissolved constituents the sample should be filtered through a 0.45 μ membrane filter as soon as practicable after collection. Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 (3 ml per liter). Normally this amount of acid will lower the pH to 2 or 3 and should be sufficient to preserve the sample indefinitely. (See Note 1). Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

NOTE 1: It has been suggested (International Biological Program, Symposium on Analytical Methods, Amsterdam, Oct. 1966) that additional acid, as much as 25 ml of concentrated HCl/liter may be required to stabilize certain types of highly buffered samples if they are to be stored for any length of time. Therefore, special precautions should be observed for preservation and storage of unusual samples intended for trace metal analysis.

4.1.2 For the determination of suspended metals a representative volume of sample should be filtered through a 0.45 μ membrane filter. When considerable sediment is present, as little as 100 ml of a well shaken sample is filtered.

Record the volume filtered and transfer the membrane filter containing the sediment to a 250 ml Griffin beaker and add 3 ml distilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot-plate and digest the material. When the acid has evaporated, cool the beaker and watch glass and add another 3 ml of distilled HNO_3.

Cover and continue heating until the digestion is complete, generally indicated by a light colored residue. Add distilled 1:1 HCl (2 ml) to the dry residue and again warm the beaker gently to dissolve the material. Wash down the watch glass and beaker walls with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected concentrations of trace metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended". STORET parameter numbers for reporting this type of data are currently being assigned.

4.1.3 For the determination of total metals the sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50-100 ml of well mixed sample will most probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined).

Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of concentrated distilled HNO_3. Place the beaker on a hot plate and evaporate to dryness making certain that the sample does not boil. Cool the beaker and add another 3 ml portion of distilled concentrated HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary until the digestion is complete, generally indicated by a light colored residue. Add sufficient distilled 1:1 HCl and again warm the beaker to dissolve the residue. Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total". STORET parameter numbers for reporting this type of data have been assigned and are given for each metal.

4.1.4 To determine metals soluble in diluted hot HCl - HNO_3, acidify the entire sample at the time of collection with redistilled HNO_3, 5 ml/l. At the time of analysis the sample is mixed and a 100-ml aliquot transferred to a beaker or flask. Five ml of redistilled hydrochloric acid is added and the sample heated for 15 minutes on a steam bath or hot plate. After this digestion period the sample is filtered and the volume adjusted to 100 ml. The sample is then ready for analysis.

The data so obtained are significant in terms of "total" metals in the sample, with the reservation that something less than "total" is actually measured. Concentrations of metal found, especially in heavily silted samples, will be substantially higher than data obtained on only the soluble fraction. STORET parameter numbers for the storage of this type data are not available at this time.

5. Interferences

5.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium determination. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

5.1.1 Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are usually employed to increase the sensitivity of the analysis they may also be used to eliminate or reduce interferences.

6. Apparatus

6.1 Atomic absorption spectrophotometer: Any commercial atomic absorption instrument having an energy source, an atomizer burner system, a monochromater, and a detector is suitable.

6.2 Burner: A Boling burner is recommended for most aqueous solutions. A premix burner is used for organic solvents. For certain elements the nitrous oxide burner is required.

6.3 Volumetric flasks: 200 ml, for extraction with organic solvents.

6.4 Glassware: All glassware, including sample bottles, should be washed with detergent, rinsed with tap water, chromic acid, tap water, 1:1 nitric acid, tap water and distilled water in that order.

6.5 Borosilicate glass distillation apparatus.

7. Reagents

7.1 Deionized distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

7.2 Nitric acid (conc): Distill reagent grade nitric acid in a borosilicate glass distillation apparatus. Prepare a 1:1 dilution with deionized distilled water. Caution: Distillation should be performed in hood with protective sash in place.

7.3 Hydrochloric acid (1:1): Prepare a 1:1 solution of reagent grade hydrochloric acid and distilled water. Distill this mixture from a borosilicate glass distillation apparatus.

7.4 Stock metal solutions: Prepare as directed in 8.1 and under the individual metal procedures.

7.5 Standard metal solutions: Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

7.6 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations.

7.7 Special reagents for the extraction procedure.

7.7.1 Ammonium pyrrolidine dithiocarbamate solution (APDC): Dissolve 1 g APDC in 100 ml of deionized distilled water. Prepare fresh before use.

7.7.2 Hydrochloric acid, 0.3N: Mix 25 ml conc. HCl with deionized distilled water and dilute to 1 liter.

Ammonium pyrrolidine dithiocarbamate (APDC) may be obtained commercially from Fisher Scientific Company (Cat. No. A-182), K and K Labs., Inc., or Eastman Kodak.

7.7.3 Methyl isobutyl ketone (MIBK): (see Note 2)

NOTE 2: One objection to MIBK is the increased solubility in a highly acid medium. By using a 3:1 mixture of MIBK - cyclohexane the solubility in the aqueous phase is decreased without any significant change in the extraction of the various chelates or burning characteristics of the ketone. Ethyl propionate has also been found to be a suitable solvent. Benzene and kerosene are inferior to MIBK because they produce a large luminous and smoke flame. Carbon tetrachloride or chloroform may also be used; however, the enhancement is considerable less than with MIBK.

7.7.4 Sodium hydroxide, 2.5N: Dissolve 10 g NaOH in deionized distilled water and dilute to 100 ml.

8. Preparation of Standards and Calibration

8.1 Stock solutions are prepared from high purity metals, oxides or nonhygroscopic reagent grade salts using redistilled nitric or hydrochloric acids. Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1000 mg of the metal per liter.

8.2 Standard solutions are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and calibration standards in graduated amounts in the appropriate range. As the filtered samples are preserved with redistilled nitric acid (3 ml 1:1 per liter) the acid strength of the calibration standards should be similarly adjusted. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution.

8.3 For those instruments which do not read out directly in concentration a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorption of 0 to 80 percent. The correct method for plotting data derived from an atomic absorption instrument equipped with a linear readout system is to convert percent absorption to absorbance and plot the absorbance against concentration. The following relationship is used to convert absorption values to absorbance:

$$\text{absorbance} = \log(100/\%\ T) = 2 - \log \%\ T$$

$$\text{where } \%\ T = 100 - \%\ \text{absorption}$$

As the curves are frequently nonlinear, especially at high absorption values, the number of standards should be increased in that portion of the curve.

9. General Procedure for Analysis by Atomic Absorption

9.1 Differences between the models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for his particular instrument. In general, after choosing the correct hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, adjust the hollow cathode current according to the manufacturer's recommendation, light the flame and regulate the flow of fuel and oxidant, adjust the burner for maximum percent absorption and stability and balance the photometer. Run a series of standards of the element under analysis and construct working curves by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. For best results run standards each time a sample or series of samples are run.

9.2 Special Extraction Procedure: When the concentration of the metal is not sufficiently high to determine directly, or when considerable dissolved solids are present in the sample, certain of the metals may be chelated and extracted with organic solvents. Ammonium pyrrolidine dithiocarbamate (APDC) is widely used for this purpose and is particularly useful for zinc, cadmium, iron, manganese, copper, silver, lead and chromium^{+6}. Tri-valent chromium does not react with APDC unless it has first been converted to the hexavalent form[3]. Aluminum, beryllium, barium and strontium also do not react with APDC.

The most frequently used organic solvent for APDC is methyl isobutyl ketone (MIBK). Apart from the fact that the solvent should extract the chelate, it should burn and provide a stable flame. In addition, the physical properties of the solvent such as viscosity, surface tension, boiling point, and mutual solubility in an aqueous medium must be taken into account. It should not produce toxic products during combustion or give a high background in the flame (see Note 3).

NOTE 3: The methods described herein have been found to be satisfactory for natural and fresh water types of samples when used by a qualified analyst. Occasions have been reported when other types of samples (sea water, brine, etc.) have presented some problems with the extraction procedure. Therefore, users are cautioned to confirm their suitability through application on spiked samples.

9.2.1 Extraction Procedure with APDC: The following extraction procedure is a general one which may be used for the majority of metals. Manganese, however, will not be extracted unless the pH is adjusted to between 4.5 and 5.0. In addition, the manganese complex is extremely unstable and must be analyzed without delay.

a. Transfer a volume of sample (100 ml maximum) into a 250 ml Griffin beaker and adjust the volume to 100 ml with deionized distilled water.

b. Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 100 ml with deionized distilled water.

c. Adjust the pH of the samples and standards to a pH of 2.5 using a pH meter.

d. Transfer the samples and standards to a 200 ml volumetric flask and add 2.5 ml fresh APDC solution and mix.

e. Add 10.0 ml MIBK and shake vigorously for one minute.

f. Allow the layers to separate and add deionized distilled water until the ketone layer is completely in the neck of the flask. Centrifuge if separation is not complete.

g. Aspirate the ketone layer and record the scale readings for each standard and sample against the prepared blank. Repeat and average the duplicate results. Plot a calibration curve in µg metal vs. absorbance (see Note 4).

NOTE 4: When aspirating organic solvents the fuel-to-air ratio should be reduced as the burning of the organic solvent contributes to the fuel supply. When adjusting the fuel-to-air ratio of the gas mixture at the burner, begin with the settings recommended by the manufacturer. Gradually reduce the fuel flow while the organic solvent is being aspirated until the flame is as blue as possible. Care should be taken that the flame does not lift off the burner producing an undesirable luminescent flame.

10. Calculation

10.1 Direct determination: Read the metal value in mg/l from the calibration curve or directly from the readout system of the instrument.

$$\text{mg/l metal in sample} = (\text{mg/l of metal in the aliquot}) \times D$$

$$\text{where } D = \frac{\text{ml of aliquot} + \text{ml of deionized distilled water}}{\text{ml of aliquot}}$$

10.2 Extracted samples: Read the metal value in µg from the extracted calibration curve or from the readout system of the instrument.

$$\text{mg/l metal in sample} = \frac{\mu\text{g metal in aliquot}}{\text{ml of aliquot}}$$

11. Precision and Accuracy

11.1 Three synthetic unknown samples containing varying concentrations of cadmium, chromium, copper, iron, lead, magnesium, manganese, silver, and zinc were analyzed in 59 laboratories with the results indicated in Table 2. (Analytical Reference Service PHS).

Table 2

Precision and Accuracy Data for Atomic Absorption Methods

Metal	Metal Concentration, µg/l	Relative Error, percent	Relative Standard Deviation, percent
Direct determination			
Cadmium	50	8.15	21.62
Chromium	50	2.29	26.44
Copper	1000	3.42	11.23
Iron	300	0.64	16.53
Magnesium	200	6.30	10.49
Manganese	50	6.00	13.50
Silver	50	10.57	17.47
Zinc	500	0.41	8.15
Extracted samples			
Cadmium	10	3.03	72.77
Lead	50	19.00	23.46

References:

(1) Atomic Absorption Newsletter, 7, 35 (1968).
(2) Spectrochim Acta, 24B, 53 (1969).
(3) Atomic Absorption Newsletter, 6, 128 (1967).

ALUMINUM

STORET NO:
DISSOLVED: 01105
TOTAL : 01107

(Standard Conditions)

Optimum Concentration Range 10-1000 mg/l using the 3092 A line

Sensitivity 0.4 mg/l

Detection Limit 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 gram of aluminum metal (analytical reagent grade). Add 15 ml of concentrated HCl to the metal in a covered beaker and warm gently. When solution is complete, transfer quantitatively to 1 liter volumetric flask and make up to volume with distilled water. One ml equals 1 mg Al.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Aluminum hollow cathode lamp
2. Wavelength: 3092 A
3. Type of burner: Nitrous oxide
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame; Fuel rich
7. Photomultiplier tube: IP-28

Notes

1. The following lines may also be used:

   3082 A Relative Sensitivity 1

   3962 A Relative Sensitivity 2

   3944 A Relative Sensitivity 2.5

ARSENIC

(Standard Conditions)

STORET NO:
DISSOLVED: 01000
TOTAL : 01002

Optimum Concentration Range 10-100 mg/1 using the 1937 A line

Sensitivity 1.0 mg/1

Detection Limit 0.5 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.320 grams of arsenic trioxide (As_2O_3, analytical reagent grade) in a small quantity of distilled water in which a pellet of NaOH has previously been dissolved. When solution is complete acidify with HCl and make up to 1 liter with distilled water. One ml equals 1 mg As (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.

Instrumental Parameters (General)

1. Arsenic hollow cathode lamp
2. Wavelength: 1937 A
3. Type of burner: Nitrous oxide
4. Fuel: Acetylene
5. Oxidant: Nitrous oxide
6. Type of flame: Fuel rich
7. Photomultiplier tube: R-106

Notes

1. The R-106 photomultiplier tube is more sensitive to UV light and therefore is suggested in place of the 1P-28 phototube.
2. Arsenic may also be determined using an air-acetylene system; however, the detection limit is 3-5 mg/1. Using an argon-hydrogen system this limit may be lowered to 0.25 mg/1; however, both chloride and nitrate ions interfere.

3. Samples high in total salt content (above 1%) will produce an apparent absorption at the 1937 A arsenic line even when the element is absent using the air-acetylene system.
4. The high-solids burner is reported to give lower detection limits with both the argon-hydrogen and air-acetylene systems.
5. The silver diethyldithiocarbamate colorimetric method is suggested for low levels of arsenic.

CADMIUM

(Standard Conditions)

STORET NO:
DISSOLVED: 01025
TOTAL : 01027

Optimum Concentration Range 0.1-1 mg/l using the 2288 A line

Sensitivity 0.004 mg/l

Detection Limit 0.001 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.142 grams of cadmium oxide (CdO, analytical reagent grade) and dissolve in 5 ml redistilled HNO_3. Dilute to 1 liter with distilled water. One ml equals 1 mg Cd.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Cadmium hollow cathode lamp
2. Wavelength: 2288 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

CALCIUM
(Standard Conditions)

STORET NO:
DISSOLVED: 00915

Optimum Concentration Range 1.0-200 mg/l using the 4227 A line

Sensitivity 0.07 mg/l

Detection Limit 0.003 mg/l

Preparation of Standard Solution

1. Stock Solution: Suspend 1.250 grams of $CaCO_3$ (analytical reagent grade), dried at 180°C for 1 hour before weighing, in distilled water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1000 ml with distilled water. One ml equals 0.5 mg of Ca (500 mg/l).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 ml concentrated HCl, (Caution! Reaction is violent) and dilute to 500 ml with distilled water.
3. Prepare dilutions of the stock calcium solutions to be used as calibration standards at the time of analysis. To each calibration standard solution, add 1.0 ml of $LaCl_3$ solution for each 10 ml of volume of working standard, ie., 20 ml working standard + 2 ml $LaCl_3$ = 22 ml.

Instrumental Parameters (General)

1. Calcium hollow cathode lamp
2. Wavelength: 4227 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Reducing
7. Photomultiplier tube: IP-28

Notes

1. Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Since low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/l also cause low calcium values. Concentrations of up to 500 mg/l each of sodium, potassium and nitrate cause no interference.
2. Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.
3. The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the samples and standards. The analysis appears to be free from chemical supressions in the nitrous oxide - acetylene flame.
4. The 2399 A line may also be used. This line has a sensitivity of 20 mg/l.

CHROMIUM

(Standard Conditions)

STORET NO:
DISSOLVED: 01030
TOTAL : 01034

Optimum Concentration Range 1.0-200 mg/l using the 3579 A line

Sensitivity 0.02 mg/l

Detection Limit 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 gram of chromium trioxide (CrO_3, reagent grade) in distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with distilled water. One ml equals 1 mg chromium.
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Chromium hollow cathode lamp
2. Wavelength: 3579 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Slightly fuel rich
7. Photomultiplier tube: IP-28

Notes

1. The following wavelengths may also be used:

3605 A Relative Sensitivity 1.2
3593 A Relative Sensitivity 1.4
4254 A Relative Sensitivity 2
4274 A Relative Sensitivity 3
4289 A Relative Sensitivity 4

2. The determination of chromium requires a rich acetylene flame. The absorption is very sensitive to the fuel-to-air ratio.
3. The absorption of chromium is suppressed by iron and nickel. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced. The interference does not exist in a nitrous oxide - acetylene flame.
4. For low levels of chromium the extraction procedure (MIBK-APDC) is recommended. Only hexavalent chromium will react with APDC, thus, to measure trivalent chromium an oxidation step must be included. (See ref. 3).

COPPER

(Standard Conditions)

STORET NO:
DISSOLVED: 01040
TOTAL : 01042

Optimum Concentration Range 0.1-10 mg/l using the 3247 A line

Sensitivity 0.04 mg/l

Detection Limit 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 gram of electrolytic copper (analytical reagent grade). Dissolve in 5 ml redistilled HNO_3 and make up to 1 liter with distilled water. Final concentration is 1 mg Cu per ml (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Copper hollow cathode lamp
2. Wavelength: 3247 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. For copper concentrations below 0.05 mg/l, the extraction procedure is suggested.
2. Copper atoms are distributed over a wider area in laminar flow-flames than that normally found. Consequently, the burner parameters are not as critical as for most other elemental determinations.

3. Because of the spectral intensity of the 3247 A line, the P.M. tube may become saturated. If this situation occurs the current should be decreased.

4. Numerous absorption lines are available for the determination of copper. By selecting a suitable absorption wavelength, copper samples may be analyzed over a very wide range of concentration. The following lines may be used:

   3264 A Relative Sensitivity 2
   2178 A Relative Sensitivity 4
   2165 A Relative Sensitivity 7
   2181 A Relative Sensitivity 9
   2225 A Relative Sensitivity 20
   2024 A Relative Sensitivity 20
   2492 A Relative Sensitivity 90

IRON

(Standard Conditions)

STORET NO:
DISSOLVED: 01046
TOTAL : 01045

Optimum Concentration Range 0.1-20 mg/l using the 2483 A line

Sensitivity 0.006 mg/l

Detection Limit 0.004 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 gram of pure iron wire (analytical reagent grade) and dissolve in 5 ml redistilled HNO_3, warming if necessary. When solution is complete make up to 1 liter with distilled water. One ml equals 1 mg Fe (1000 mg/l).
2. Prepare dilutions of the stock solutions to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Iron hollow cathode lamp
2. Wavelength: 2483 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. The following lines may also be used:

   2488 A Relative Sensitivity 2
   2522 A Relative Sensitivity 2
   2719 A Relative Sensitivity 4
   3021 A Relative Sensitivity 5

2527 A Relative Sensitivity 6
2721 A Relative Sensitivity 9
3720 A Relative Sensitivity 10
2967 A Relative Sensitivity 12
3860 A Relative Sensitivity 20
3441 A Relative Sensitivity 30

2. Absorption is strongly dependent upon the lamp current.
3. Better signal-to-noise can be obtained from a neon-filled hollow cathode lamp than from an argon-filled lamp.

LEAD

(Standard Conditions)

STORET NO:
DISSOLVED: 01049
TOTAL : 01051

Optimum Concentration Range 1-10 mg/l using the 2170 A line

Sensitivity 0.06 mg/l

Detection Limit 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.599 gram of analytical reagent grade lead nitrate $[Pb(NO_3)_2,]$ and dissolve in redistilled water. When solution is complete acidify with 10 ml redistilled HNO_3 and dilute to 1 liter with distilled water. One ml equals 1 mg Pb (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Lead hollow cathode lamp
2. Wavelength: 2170
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Slightly oxidizing
7. Photomultiplier tube: IP-28

Notes

1. The analysis of this metal is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of

the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.

2. Better analytical results with the 2170 A line may be obtained by using a R-106 photomultiplier tube which is more sensitive to UV light.
3. For lead concentrations below 0.2 mg/1, the extraction procedure is suggested. The optimum pH for the extraction is 2.8.
4. The following lines may also be used:

   2833 A Relative Sensitivity 2

   2614 A Relative Sensitivity 500

   3683 A Relative Sensitivity 900

MAGNESIUM

STORET NO:
DISSOLVED: 00925
TOTAL : 00927

(Standard Conditions)

Optimum Concentration Range 0.01-2 mg/l using the 2852 A line

Sensitivity 0.005 mg/l

Detection Limit 0.0005 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade) in 10 ml of redistilled HNO_3 and dilute to 1 liter with distilled water. One ml equals 0.50 mg.
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3, slowly and in small portions in 250 ml concentrated HCl, (Caution! Reaction is violent) and dilute to 500 ml with distilled water.
3. Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. To each calibration standard solution, add 1.0 ml of $LaCl_3$ solution for each 10 ml of volume of working standard, ie., 20 ml working standard + 2 ml $LaCl_3$ = 22 ml.

Instrumental Parameters (General)

1. Magnesium hollow cathode lamp
2. Wavelength: 2852 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Reducing
7. Photomultiplier tube: IP-28

Notes

1. Analytical sensitivity decreases with increased lamp current.
2. The interference caused by aluminum at concentrations greater than

2 mg/l is masked by addition of lanthanum. Since low magnesium values result if the pH of the samples is above 7, both standards and samples are prepared in dilute hydrochloric acid. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/l.

3. Because of the spectral intensity of the 2852 line, the P.M. tube may become saturated. If this situation occurs, the current should be decreased.
4. The following lines may also be used:

   2025 A Relative Sensitivity 250
   7025 A Relative Sensitivity 250
   2796 A Relative Sensitivity 1000
5. To cover the range of magnesium values normally observed in surface waters (0.1-20 mg/l), it is suggested that the burner be rotated 55°.

MANGANESE

(Standard Conditions)

STORET NO:
DISSOLVED: 01056
TOTAL : 01055

Optimum Concentration Range 0.1-20 mg/l using the 2795 A line

Sensitivity 0.04 mg/l

Detection Limit 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.583 gram of analytical reagent grade manganese dioxide, MnO_2 and dissolve in 10 ml of HCl. When solution is complete dilute to 1 liter with distilled water. One ml equals 1 mg Mn (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% nitric acid in all calibration standards.

Instrumental Parameters (General)

1. Manganese hollow cathode lamp
2. Wavelength: 2795 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. For manganese concentrations below 0.01 mg/l, the extraction procedure is suggested. The extraction is carried out at pH 4.5-5. The manganese chelate is very unstable and the analysis must be made without delay to prevent its re-solution in the aqueous phase.
2. Analytical sensitivity is somewhat dependent on lamp current.

POTASSIUM

(Standard Conditions)

STORET NO:
DISSOLVED: 00935
TOTAL : 00937

Optimum Concentration Range 0.01-2 mg/l using the 7665 A line

Sensitivity 0.01 mg/l

Detection Limit 0.005 mg/l

Preparation of Standard Solutions

1. Stock Solution: Dissolve 0.1907 grams of KCl (analytical reagent grade), dried at 110°C, in distilled water and make up to 1 liter. One ml equals 0.10 mg of potassium (100 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.

Instrumental Parameters (General)

1. Potassium hollow cathode lamp
2. Wavelength: 7665 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Slightly oxidizing
7. Photomultiplier tube: IP-21

Notes

1. If an IP-21 photodetector tube is not available, the IP-28 may be used. This will result in some loss of sensitivity.
2. The Osram potassium vapor-discharge lamp may also be used in the Perkin-Elmer 303. In this case the lamp current should be 350 ma or the optimum operating current.
3. Sodium may interfere if present at much higher levels than the potassium. This effect can be avoided by approximately matching the

sodium content of the potassium standards with that of the sample.

4. Potassium absorption is enhanced in the presence of Na, Li and Cs, especially in a high-temperature flame. This enhancement effect of sodium can be eliminated by changing the burner height and the type of flame used. The burner assembly is set approximately 0.05 cm below the optical light path so that the optical light path is sliced at the bottom by the burner head. A fuel-rich flame is used (303-burner, airflow 7.5, acetylene flow 9.0).
5. The 4044 A line may also be used. This line has a sensitivity of 5 mg/l for 1% absorption.
6. To cover the range of potassium values normally observed in surface waters (0.1-20 mg/l), it is suggested that the burner be rotated 75°.

SILVER

(Standard Conditions)

STORET NO:
DISSOLVED: 01075
TOTAL : 01077

Optimum Concentration Range 0.1-20 mg/l using the 3281 A line

Sensitivity 0.05 mg/l

Detection Limit 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in distilled water, add 10 ml HNO_3 and make up to 1 liter. One ml equals 1 mg of silver (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% HNO_3 in all calibration standards.

Instrumental Parameter (General)

1. Silver hollow cathode lamp
2. Wavelength: 3281 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. The 3382 A line may also be used. This line has a relative sensitivity of 3.
2. Silver nitrate standards are light sensitive. Dilutions of the stock should be discarded after use as concentrations below 10 mg/l are not stable over long periods of storage.

SODIUM

(Standard Conditions)

STORET NO:
DISSOLVED: 00930
TOTAL : 00929

Optimum Concentration Range 1.0-200 mg/l using the 3302 A line

Sensitivity 0.003 mg/l

Detection Limit 0.001 mg/l

Preparation of Standard Solutions

1. Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in distilled water and make up to 1 liter. One ml equals 1 mg of sodium (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.

Instrumental Parameters (General)

1. Sodium hollow cathode lamp
2. Wavelength: 3302 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. For the Perkin-Elmer instrument the "290" burner is used to increase the concentration range of sodium using the most sensitive line 5890. The burner is installed perpendicular (rotated 90°) to the light path. The upper concentration limit is 60 mg/l without sample dilution.
2. The 3302 A resonance line of sodium yields a sensitivity of about 5 mg/l sodium for 1% absorption and provides a convenient way to

SODIUM

(Standard Conditions)

STORET NO:
DISSOLVED: 00930
TOTAL : 00929

Optimum Concentration Range 1.0-200 mg/l using the 3302 A line

Sensitivity 0.003 mg/l

Detection Limit 0.001 mg/l

Preparation of Standard Solutions

1. Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in distilled water and make up to 1 liter. One ml equals 1 mg of sodium (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.

Instrumental Parameters (General)

1. Sodium hollow cathode lamp
2. Wavelength: 3302 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. For the Perkin-Elmer instrument the "290" burner is used to increase the concentration range of sodium using the most sensitive line 5890. The burner is installed perpendicular (rotated 90°) to the light path. The upper concentration limit is 60 mg/l without sample dilution.
2. The 3302 A resonance line of sodium yields a sensitivity of about 5 mg/l sodium for 1% absorption and provides a convenient way to

avoid the need to dilute more concentrated solutions of sodium.

3. Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal.
4. For more sensitivity the IP-21 photomultiplier tube and the 5890 A line may be used to extend the range to 0.005-0.2 mg/l.

ZINC

(Standard Conditions)

STORET NO:
DISSOLVED: 01090
TOTAL : 01092

Optimum Concentration Range 0.1-2 mg/l using the 2139 A line

Sensitivity 0.02 mg/l

Detection Limit 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 gram of analytical reagent grade zinc metal and dissolve cautiously in 10 ml HNO_3. When solution is complete make up to 1 liter with distilled water. One ml equals 1 mg Zn (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Maintain an acid strength of 0.15% HNO_3 in all calibration standards.

Instrumental Parameters (General)

1. Zinc hollow cathode lamp
2. Wavelength: 2139 A
3. Type of burner: Boling
4. Fuel: Acetylene
5. Oxidant: Air
6. Type of flame: Oxidizing
7. Photomultiplier tube: IP-28

Notes

1. High levels of silicon may interfere.
2. The air-acetylene flame absorbs about 25% of the energy at the 2139 A line.
3. The sensitivity may be increased by the use of low-temperature flames.

MERCURY

(Flameless AA Procedure)

STORET NO.
Total: 71900
Dissolved: 71890

1. Scope and Application

1.1 This method is applicable to surface waters, saline waters, wastewaters and effluents.

1.2 With proper digestion other materials such as fish tissue, mud and sediments may also be analyzed using the described technique (see Appendix 11.1 and 11.2).

1.3 In addition to inorganic forms of mercury, organic mercurials may also be present in an effluent or surface water sample. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this method.

Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.

1.4 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 µg Hg/l can be achieved; concentrations below this level should be reported as <0.2 (see Appendix 11.4).

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection(1). If only dissolved mercury is to be determined, the sample should be filtered before the acid is added. For total mercury the filtration is omitted.

4. Interference

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on the recovery of mercury from spiked samples.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step chlorides are converted to free chlorine which will also absorb radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present (see Appendix 11.3).

5. Apparatus

5.1 Atomic Absorption Spectrophotometer*: Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL - 22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. x 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter x 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

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*Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.8 Drying Tube: 6" x 3/4" diameter tube containing 20 grams of magnesium perchlorate (see Note 1.) The apparatus is assembled as shown in the accompanying diagram.

NOTE 1: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade

6.1.1 Sulfuric acid, 1.0 N: Dilute 28.0 ml of conc. sulfuric acid to 1.0 liter.

6.1.2 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content.

NOTE 2: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride and hydroxylamine hydrochloride may also be used.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 grams of sodium chloride and 12 grams of hydroxylamine sulfate in distilled water and dilute to 100.0 ml.

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 grams of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 grams of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 grams of mercuric chloride in 75 ml of distilled water. Add 10 ml of concentrated nitric acid and adjust the volume to 100.0 ml. 1 ml = 1 mg Hg.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 1.0, 2.0 and 5.0 ml aliquots of the working mercury solution containing 0 to 0.5 µg of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of concentrated sulfuric acid and 2.5 ml of nitric acid to each bottle.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride and hydroxylamine hydrochloride may also be used.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 grams of sodium chloride and 12 grams of hydroxylamine sulfate in distilled water and dilute to 100.0 ml.

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 grams of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 grams of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 grams of mercuric chloride in 75 ml of distilled water. Add 10 ml of concentrated nitric acid and adjust the volume to 100.0 ml. 1 ml = 1 mg Hg.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 1.0, 2.0 and 5.0 ml aliquots of the working mercury solution containing 0 to 0.5 µg of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of concentrated sulfuric acid and 2.5 ml of nitric acid to each bottle.

NOTE 4: Loss of mercury may occur at elevated temperatures. However, with the stated amounts of acid the temperature rise is only 13°C (25 → 38°C) and no losses of mercury were observed.

Add 1 ml of $KMnO_4$ solution to each bottle and allow to stand at least 15 minutes. Add 2 ml of potassium persulfate to each bottle and allow to stand for at least 30 minutes additional. Add 2 ml of sodium chloride - hydroxylamine sulfate solution to reduce the excess permanganate. Treating each bottle individually, add 5 ml of the stannous sulfate solution and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously.

The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

8. Procedure

8.1 Transfer 100 ml or an aliquot diluted to 100 ml containing not more than 0.5 μg of mercury to a 300 ml BOD bottle. Add 5 ml of sulfuric acid and 2.5 ml of nitric acid mixing after each addition (see Note 4 under 7). Add 1 ml of potassium permanganate solution (6.5) to each sample bottle. Shake and add additional portions of potassium permanganate solution (6.5) until the purple color persists for at least 15 minutes. Add 2 ml of potassium persulfate to each bottle and allow to stand an additional 30 minutes. Add sodium chloride-hydroxylamine sulfate in 2 ml increments to reduce the excess permanganate. Add 5 ml of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu g\,Hg/l = \underset{\text{in aliquot}}{\mu g\ Hg} \times \frac{1000}{\text{volume of aliquot}}$$

9.3 Report mercury concentrations as follows:

Below 0.2 μg/l, <0.2; between 1 and 10 μg/l, one decimal; above 10 μg/l, whole numbers.

10. Precision and Accuracy

10.1 Using an Ohio River composite sample with a background mercury concentration of 0.35 μg/l, spiked with concentrations of 1, 3 and 4 µg/l, the standard deviations were ±0.14, ±0.10 and ±0.08, respectively. Standard deviation at the 0.35 level was ±0.16. Percent recoveries at the three levels were 89, 87, and 87%, respectively.

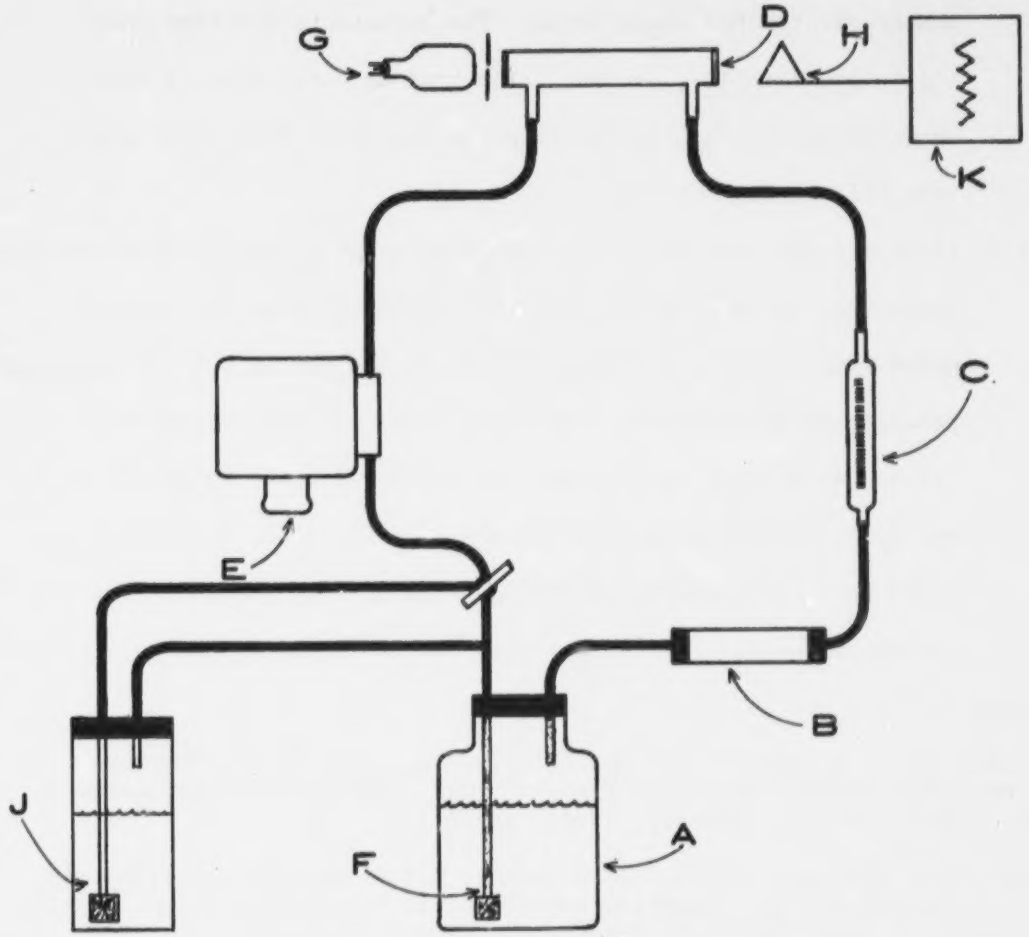
11. Appendix

11.1 For the measurement of mercury in fish tissue, the procedure of Uthe, Armstrong, and Stainton(2) was found to be satisfactory. The digestion step is carried out directly in the BOD bottle. After the potassium permanganate oxidation step, the volume of the digest is adjusted to approximately 100 ml with distilled water and the same procedure followed as used for water samples.

11.2 For the analysis of mud and sediment samples a vigorous digestion using a water cooled reflux condenser approximately 2 feet in length is used. A 5.0 gram sample is placed in a 250 ml round bottom flask and fitted to the condenser. Add 10 ml of redistilled nitric acid and apply heat using a heating mantle until the acid refluxes gently. Continue heating for 2 hours and cool the mixture. Wash down the column with about 60 - 70 ml of distilled water. Filter the sample through Whatman No. 42 paper to remove the insoluble material and make the filtrate up to 100 ml with distilled water. Take a suitable aliquot for analysis and proceed as described under the procedure for water samples. If an aliquot of less than 25 ml is taken for analysis, additional nitric acid is added to make a total of 2.5 ml.

11.3 While the possibility of absorption from certain organic substances actually being present in the sample does exist, the AQC Laboratory has not encountered such samples. This is mentioned only to caution the analyst of the possibility. A simple correction that may be used is as follows:

SCHEMATIC ARRANGEMENT OF EQUIPMENT FOR MERCURY MEASUREMENT BY COLD VAPOR AA TECHNIQUE



A - Sample container, approximately 300 ml (BOD bottle)
B - Drying tube, 150-200 ml capacity with $MgClO_4$
C - Rotameter, ≈ 1 liter of air/minute
D - Cell, with quartz windows
E - Air pump, ≈ 1 liter of air/minute
F - Glass tube with fritted end
G - Hollow cathode Hg Lamp
H - AA Detector
J - Gas washing bottle containing 0.25% iodine in a 3% potassium iodide solution
K - Recorder, any compatible model

METHYLENE BLUE ACTIVE SUBSTANCES (MBAS)

(Methylene Blue Method)

STORET NO. 38260

1. Scope and Application

1.1 This method is applicable to the measurement of methylene blue active substances (MBAS) in drinking waters, surface waters, domestic and industrial wastes. It is not applicable to measurement of surfactant-type materials in saline waters.

1.2 It is not possible to differentiate between linear alkyl sulfonate (LAS) and alkyl benzene sulfonate (ABS) or other isomers of this type compounds. However, LAS has essentially replaced ABS on the surfactant market so that measurable surfactant materials will probably be LAS type materials.

1.3 The method is applicable over the range of 0.025 to 100 mg/1 LAS.

2. Summary of Method

2.1 The dye, methylene blue, in aqueous solution reacts with anionic-type surface active materials to form a blue colored salt. The salt is extractable with chloroform and the intensity of color produced is proportional to the concentration of MBAS.

3. Comments

3.1 Materials other than man-made surface active agents which react with methylene blue are organically bound sulfates, sulfonates, carboxylantes, phosphates, phenols, cyanates, thiocyanates and some inorganic ions such as nitrates and chlorides. However, the occurrence of these materials at interference levels is relatively rare and with the exception of chlorides may generally be disregarded.

3.2 Chlorides at concentration of about 1000 mg/l show a positive interference but the degree of interference has not been quantified. For this reason the method is not applicable to brine samples.

3.3 Naturally occurring organic materials that react with methylene blue are relatively insignificant. Except under highly unusual circumstances, measurements of MBAS in finished waters, surface waters and domestic sewages may be assumed to be accurate measurements of man-made surface active agents.

4. Precision and Accuracy

4.1 On a sample of filtered river water, spiked with 2.94 mg LAS/liter, 110 analysts obtained a mean of 2.98 mg liter with a standard deviation of 0.272.

4.2 On a sample of tap water spiked with 0.48 mg LAS/liter, 110 analysts obtained a mean of 0.49 mg/l with a standard deviation of 0.048.

4.3 On a sample of distilled water spiked with 0.27 mg LAS/liter, 110 analysts obtained a mean of 0.24 mg/l with a standard deviation of 0.036.

4.4. Analytical Reference Service, Water Surfactant No. 3, Study No. 32, (1968).

5. References

The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewaters, 13th Edition, pp 339-342, Method No. 159A (1971).

American Society for Testing and Materials, Part 23, Method D2330-68, pp 721-727, (1970).

NITROGEN-AMMONIA

(Distillation Procedure)

STORET NO. 00610

1. Scope and Application

1.1 This distillation method covers the determination of ammonia-nitrogen, exclusive of total Kjeldahl nitrogen, in surface waters, domestic and industrial wastes, and saline waters. It is the method of choice where economics and sample load do not warrant the use of automated equipment.

1.2 The method covers the range from about 0.05 to 1.0 mg/l NH_3/N per liter for the colorimetric procedures and from 1.0 to 25 mg/l for the titrimetric procedure.

1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.

2. Summary of Method

2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined either colorimetrically by nesslerization or titrimetrically with standard sulfuric acid with the use of a mixed indicator, the choice between these two procedures depending on the concentration of the ammonia.

3. Sample Handling and Preservation

3.1 Until more conclusive data is obtained samples may be preserved by addition of 40 mg $HgCl_2$ per liter and stored at 4°C. If only ammonia is to be determined on the sample it may be preserved with 1.0 ml of concentrated H_2SO_4 per liter and stored at 4°C.

4. Interferences

4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.

4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds such as hydrazine will influence the titrimetric results. Some volatile compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.

4.3 Residual chlorine must also be removed by pre-treatment of the sample with sodium thiosulfate before distillation.

4.4 If the sample has been preserved with a mercury salt, the mercury ion must be complexed with sodium thiosulfate prior to distillation.

5. Apparatus

5.1 An all-glass distilling apparatus with an 800-1000 ml flask.

5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.

5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm ±1.5 mm inside measurement from bottom.

5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

6.2 Ammonium chloride, stock solution, (1.0 ml = 1.00 mg NH_3-N). Dissolve 3.819 g NH_4Cl in water and bring to volume in a 1 liter volumetric flask.

6.3 Ammonium chloride, standard solution, (1.0 ml = 0.01 mg). Dilute 10 ml of this stock solution to 1 liter in a volumetric flask for use as the standard ammonium chloride solution.

6.4 Boric acid solution (20 g/l) - Dissolve 20 g H_3BO_3 in water and dilute to 1 liter.

6.5 Mixed indicator - Mix 2 volumes of 0.2 percent methyl red in 95 percent ethyl alcohol with 1 volume of 0.2 percent methylene blue in 95 percent ethyl alcohol. This solution should be prepared fresh every 30 days. Note 1 - Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95 percent ethanol.

6.6 Nessler reagent - Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

Note 2 - This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).

6.7 Borate buffer - Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g $Na_2B_4O_7$ per liter) and dilute to 1 liter.

6.8 Sulfuric acid, standard solution, (0.02 N, 1 ml = 0.28 mg NH_3-N). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of concentrated H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1 liter with CO_2-free distilled water.

Note 3 - An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.0200 N acid can then be prepared.

6.9 Sodium hydroxide, 1 N. Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.10 Dechlorinating reagents. A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

(a) Sodium thiosulfate (1/70 N): Dissolve 3.5 g $Na_2S_2O_3$ in ammonia-free water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.

(b) Sodium arsenite (1/70 N): Dissolve 1.0 g $NaAsO_2$ in ammonia-free water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment - Add 500 ml of ammonia-free water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation - To 400 ml of sample add 1 N NaOH until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation - Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer. Distill 300 ml at the rate of 6-10 ml/min. into 50 ml of 2% boric acid contained in a 500 ml glass stoppered Erlenmeyer flask. Dilute the distillate to 500 ml in the flask and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1.0 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically.

7.4 Determination of ammonia in distillate - Determine the ammonia content of the distillate either titrimetrically or colorimetrically as described below. (See 7.4.1 and 7.4.2).

7.4.1 Titrimetric determination. Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, matching the end point against a blank containing the same volume of ammonia-free water and H_3BO_3 solution.

7.4.2 Colorimetric determination. Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3N	Conc., When Diluted to 50.0 ml, mg NH_3N/liter
0.0 (Blank)	0.0
0.2	0.04
0.5	0.10
1.0	0.20
1.5	0.30
2.0	0.40
3.0	0.60
4.0	0.80

Dilute each tube to 50 ml with ammonia-free water, add 1.0 ml of Nessler reagent and mix. After 20 minutes read the optical densities at 425 nm against the blank. From the values obtained plot optical density (absorbance) vs. concentration for the standard curve.

7.4.3 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

7.5 Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the optical density at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

8. Calculations

8.1 Titrimetric

$$\text{mg/l } NH_3N = \frac{A \times 0.28 \times 1000}{S}$$

in which:

A = ml 0.02 N H_2SO_4 used

S = ml sample

8.2 Spectrophotometric

$$\text{mg/l } NH_3N = \frac{A \times 1000}{0.8\ S}$$

in which:

A = NH_3N read from standard curve

S = volume of distillate nesslerized

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

Increment as Nitrogen, Ammonia mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/Liter
.21	0.122	- 5.54	-.01
.26	0.070	-18.12	-.05
1.71	0.244	+ 0.46	+.01
1.92	0.279	- 2.01	-.04

(FWPCA Method Study 2, Nutrient Analyses)

NITROGEN, AMMONIA

(Automated Method)

STORET NO. 00610

1. Scope and Application

   1.1 This method pertains to the determination of ammonia present in surface and saline waters. Depending upon the selection of the size of flow cell, and extent of dilution, concentrations in the range between .01 and 20 mg/liter N present as NH_3 may be determined.

2. Summary of Method

   2.1 The intensity of the indophenol blue color(1), formed by the reaction of ammonia with alkaline phenol hypochlorite, is measured. Sodium nitroprusside is used to intensify the blue color.

3. Sample Handling and Preservation

   3.1 Preservation by addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C. Note $HgCl_2$ interference under 4.3.

4. Interferences

   4.1 In sea water, calcium and magnesium ions are present in concentrations sufficient to cause precipitation problems during the analysis. This problem is eliminated by using 5% EDTA.

   4.2 Any marked variation in acidity or alkalinity among samples should be eliminated, since the intensity of the color used to quantify the concentration is pH dependent. Likewise, the pH of the wash water and the standard ammonia solutions should approximate that of the samples. For example, if the samples have been preserved with 1 ml concentrated H_2SO_4/liter, the wash water and standards should also contain 1 ml conc. H_2SO_4/l.

   4.3 Mercury chloride, used as a preservative, gives a negative interference by complexing with the ammonia. This is overcome by adding a comparable amount of $HgCl_2$ to the ammonia standards used for the preparation of the standard curve.

5. Apparatus

5.1 Technicon AutoAnalyzer Unit consisting of:

5.1.1 Sampler.

5.1.2 Manifold.

5.1.3 Proportioning pump.

5.1.4 Heating bath with double delay coil.

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 630 or 650 nm filters.

5.1.6 Recorder.

6. Reagents

6.1 Distilled Water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Since organic contamination may interfere with this analysis, use of the resin Dowex XE-75 or equivalent which also tends to remove organic impurities is advised. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer.

6.2 Segmenting Fluid: Air scrubbed with 5N H_2SO_4. Ammonia free concentrated sulfuric acid and ammonia free distilled water used in the acid preparation.

6.3 Sodium Phenolate: Using a 1 liter Erlenmeyer flask, dissolve 83 g phenol in 500 ml distilled water. In small increments, cautiously add with agitation, 32 g of NaOH. Periodically, cool flask under water faucet. When cool, dilute to 1 liter.

6.4 Sodium Hypochlorite Solution ("Clorox"): Dilute 250 ml of 5% "Clorox" to 500 ml with distilled water. Available chlorine level should approximate 2 to 3%. Since "Clorox" is a proprietary product and its formulation is subject to change, the analyst must remain alert to detecting any variation in this product significant to its use in this procedure.

6.5 EDTA (5%): Dissolve 50 g of EDTA (disodium salt) and approximately six pellets of NaOH in 1 liter of ammonia-free water.

Note: On salt water samples where EDTA solution does not prevent precipitation of cations, sodium potassium tartrate solution may be used to advantage. It is prepared as follows:

6.5.1 Sodium Potassium Tartrate Solution: 10% $NaKC_4H_4O_6$. To 900 ml distilled water add 100 g sodium potassium tartrate. Add 2 pellets of NaOH and a few boiling chips, boil gently for 45 minutes. Cover, cool, and dilute to 1 liter. Adjust pH to 5.2 ± .05 with H_2SO_4. After allowing to settle overnight in a cool place, filter to remove precipitate. Then add 1/2 ml Brij-35* solution and store in stoppered bottle.

6.6 Sodium Nitroprusside (0.05%): Dissolve 0.5 g of sodium nitroprusside in 1 liter of ammonia-free water.

6.7 Stock Solution: Dissolve 3.819 g of anhydrous ammonium chloride, NH_4Cl, dried at 105°C, in ammonia-free water, and dilute to 1 liter. 1 ml = 1.0 mg NH_3N.

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*Available from Technicon Corporation.

6.8 Standard Solution A: Dilute 10.0 ml of stock solution to 1 liter with ammonia-free water. 1 ml = .01 mg NH_3N.

6.9 Standard Solution B: Dilute 10.0 ml of standard solution A to 100 ml with ammonia-free water. 1 ml = .001 mg NH_3N.

6.10 Using standard solutions A and B, prepare the following standards in 100 ml volumetric flasks (prepare fresh daily):

NH_3N, mg/l	ml Standard Solution/100 ml
	Solution B
0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0
	Solution A
0.20	2.0
0.50	5.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

Note: When saline water samples are analyzed, Substitute Ocean Water (SOW) should be used for preparing the above standards used for the calibration curve; otherwise, distilled water is used. If SOW is used, determine its blank background.

Substitute Ocean Water (SOW)

	g./l.		g./l.
NaCl	24.53	$NaHCO_3$	0.20
$MgCl_2$	5.20	KBr	0.10
Na_2SO_4	4.09	H_3BO_3	0.03
$CaCl_2$	1.16	$SrCl_2$	.03
KCl	0.70	NaF	.003

7. Procedure

7.1 For a working range of 0.01 to 2.00 NH_3N mg/1, set up the manifold as shown in Figure 1. Higher concentrations may be accommodated by decreasing sample size and/or through dilution of sample.

7.2 Allow both colorimeter (with 650 nm filters and 15 mm flow cell) and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding ammonia-free water through sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place a distilled water wash tube in alternate openings in sampler and set sample timing at 2.0 minutes. All tubes must be rinsed with ammonia-free water before use.

7.4 Arrange ammonia standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculations

8.1 Prepare appropriate standard curve derived from processing ammonia standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (AQC), using surface water samples at concentrations of 1.41, 0.77, 0.59, and 0.43 mg NH_3-N/1, the standard deviation was ±0.005.

9.2 In a single laboratory (AQC), using surface water samples at concentrations of 0.16 and 1.44 mg NH_3-N/1, recoveries were 107% and 99%, respectively.

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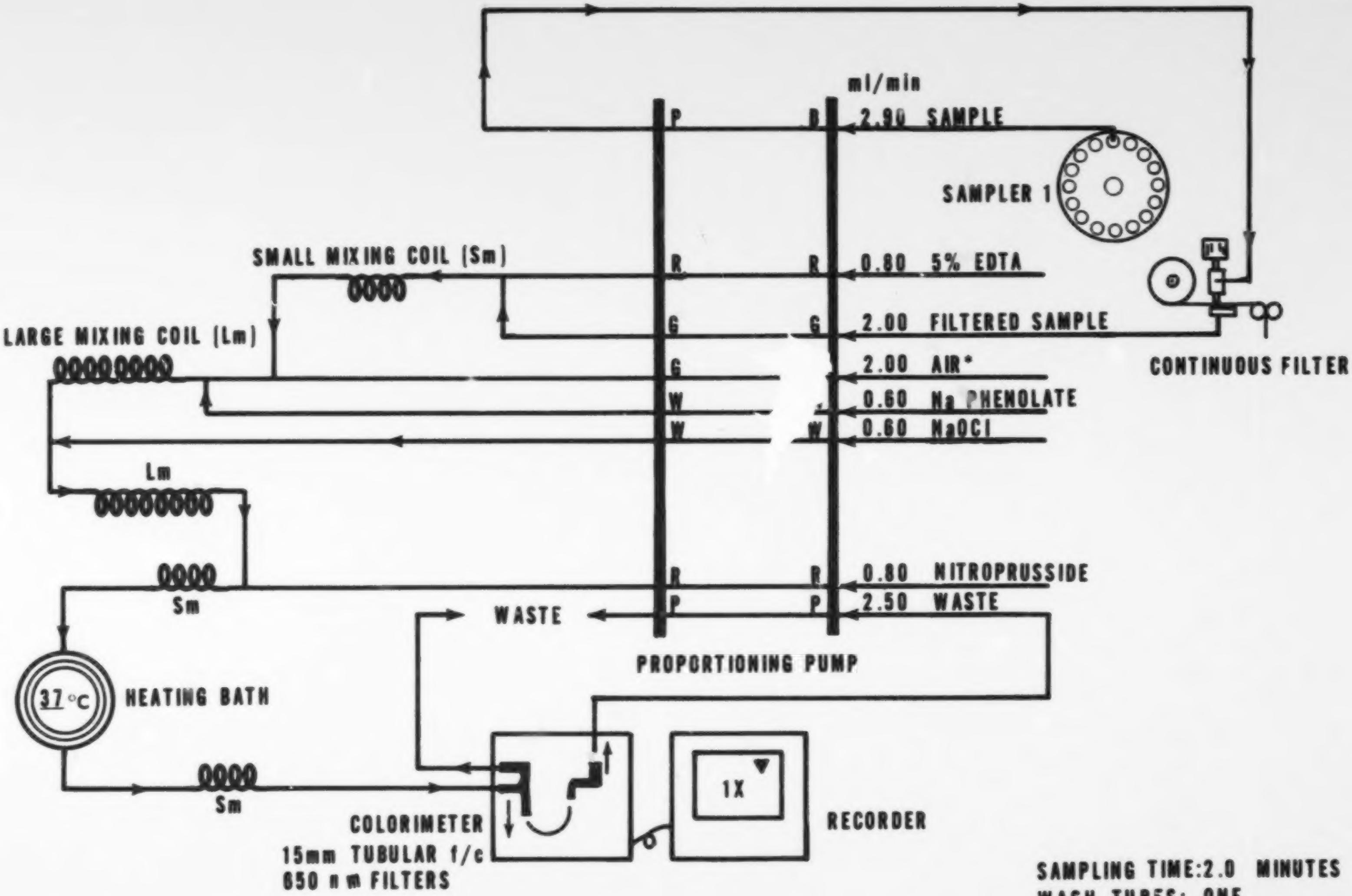
ml/min
P
B
2.90 SAMPLE
SAMPLER 1
SMALL MIXING COIL (Sm)
R
R
0.80 5% EDTA
G
G
2.00 FILTERED SAMPLE
CONTINUOUS FILTER
LARGE MIXING COIL (Lm)
G
2.00 AIR*
W
0.60 Na PHENOLATE
W
W
0.60 NaOCl
Lm
R
R
0.80 NITROPRUSSIDE
Sm
P
P
2.50 WASTE
WASTE
PROPORTIONING PUMP
37 °C
HEATING BATH
Sm
1X
COLORIMETER
15mm TUBULAR f/c
650 n m FILTERS
RECORDER

SAMPLING TIME:2.0 MINUTES
WASH TUBES: ONE

*SCRUBBED THROUGH 5N H_2SO_4

FIGURE 1. AMMONIA MANIFOLD

NITROGEN KJELDAHL, TOTAL

STORET NO. 00625

1. Scope and Application

1.1 This method covers the determination of total Kjeldahl nitrogen in surface waters, domestic and industrial wastes, and saline waters. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semi-carbazones and some refractory tertiary amines.

1.2 Two alternatives are listed for the determination of ammonia after distillation; the titrimetric method which is applicable to concentrations above 1 mg N/liter and the Nesslerization method which is applicable to concentrations below 1 mg N/liter.

1.3 This method is described for a macro system of glassware; however, micro glassware which does not change the chemistry of the procedure is equally applicable.

2. Definitions

2.1 Total Kjeldahl is defined as the sum of free ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.

2.2 Organic Kjeldahl Nitrogen is defined as the difference obtained by subtracting the free ammonia value (cf Nitrogen, Ammonia, this Manual) from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.

3. Summary of Method

3.1 The sample is heated in the presence of concentrated sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until SO_3 fumes are obtained and the

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solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation either by nesslerization or titrimetrically.

4. Sample Handling and Preservation

4.1 Samples may be preserved by addition of 40 mg $HgCl_2$/l and stored at 4°C. Even when so preserved, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.

5. Apparatus

5.1 Digestion apparatus. A Kjeldahl digestion apparatus with 800 ml flasks and suction takeoff to remove SO_3 fumes and water is required. Use of micro-Kjeldahl equipment is also permissible.

5.2 Distillation apparatus. The Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected for nesslerization or in indicating H_3BO_3 solution for titration.

5.3 Spectrophotometer for use at 400 to 425 nm with a light path of 1 cm or longer.

5.4 Nessler tubes, tall form 50 ml.

6. Reagents

6.1 Distilled waters should be free of ammonia. Such water is best prepared by the passage of distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

6.2 Mercuric sulfate solution. Dissolve 8 g red, mercuric oxide (HgO) in 50 ml of 1:5 sulfuric acid and dilute to 100 ml with distilled water.

6.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution. Dissolve 267 g K_2SO_4 in 1300 ml water and add 400 ml concentrated H_2SO_4. Add 50 ml mercuric sulfate solution and dilute to 2 liters.

6.4 Sodium hydroxide-sodium thiosulfate solution. Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 . 5H_2O$ in water and dilute to 1 liter.

6.5 Phenolphthalein indicator solution. Dissolve 5 g phenolphthalein in 500 ml 95% ethyl alcohol or isopropanol and add 500 ml water. Add 0.02 NaOH dropwise until a faint, pink color appears.

6.6 Mixed indicator. Mix 2 volumes of 0.2% methyl red in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.

6.7 Boric acid solution. Dissolve 20 g boric acid, H_3BO_3, in water and dilute to 1 liter with water.

6.8 Sulfuric acid titrant, 0.020 N. (1.00 ml = 0.28 mg N).

6.9 Ammonium chloride, stock solution (1.0 ml = 1.0 mg NH_3-N). Dissolve 3.819 g NH_4Cl in water and make up to 1.0 liter with ammonia free water.

6.10 Ammonium chloride, standard solution, (1.0 ml = 0.01 mg NH_3-N). Dilute 10.0 ml of the stock solution to 1.0 liter.

6.11 Nessler reagent - Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small volume of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. The solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight.

Note - Reagents 6.8, 6.9, 6.10, and 6.11 are identical to reagents 6.8, 6.2, 6.3, and 6.6 described under Nitrogen, Ammonia.

7. Procedure

7.1 The distillation apparatus should be pre-steamed before use by distilling a 1:1 mixture of ammonia-free water and sodium hydroxide-sodium thiosulfate solution until the distillate is ammonia free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

7.2 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800-ml Kjeldahl flask. The sample size can be determined from the following table:

Kjeldahl Nitrogen in Sample, mg/l	Sample Size ml
0 - 5	500
5 - 10	250
10 - 20	100
20 - 50	50.0
50 - 100	25.0

Dilute the sample, if required, to 500 ml, and add 100 ml sulfuric acid - mercuric sulfate - potassium sulfate solution (Note 2), and evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Cool the residue and add 300 ml water.

Note 2 - Alternately digest the sample with 1 Kel-Pac (Olin-Matheson) and 20 ml conc. H_2SO_4. Cut the end from the package and empty the contents into the digestion flask; discard the container.

7.3 Make the digestate alkaline by careful addition of the sodium hydroxide-thiosulfate solution without mixing (20 ml of 36 N H_2SO_4 requires approximately 60 ml of 12.5 N $NaOH-Na_2S_2O_3$ to neutralize).

Note - Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause the heavier solution to underlay the aqueous sulfuric acid solution without loss of free ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

7.4 Connect the Kjeldahl flask to the condenser with the tip of condenser (or an extension of the condenser tip) below the level of the boric acid solution in the receiving flask.

7.5 Distill 300 ml at the rate of 6-10 ml/min., into 50 ml of 2% boric acid contained in a 500-ml glass stoppered Erlenmeyer flask.

7.5.1 If it is anticipated that the ammonia measurement will be by nesslerization, 50 ml of boric acid is preferred. If, however, sufficient ammonia is present to permit titration of a larger volume of boric acid, either 100 or 200 ml, may be used.

7.6 Dilute the distillate to 500 ml in the flask and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1.0 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically.

7.7 Determination of ammonia in distillate - Determine the ammonia content of the distillate either titrimetrically or colorimetrically as described below.

7.7.1 Titrimetric determination. Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, matching the endpoint against a blank containing the same volume of ammonia-free water and H_3BO_3 solution.

7.7.2 Colorimetric determination. Prepare a series of Nessler tube standards as follows:

ml as Standard 1.0 ml = 0.01 mg NH_3N	Conc., When Diluted to 50.0 ml, mg NH_3N/liter
0.0 (Blank)	0.0
0.2	0.04
0.5	0.10
1.0	0.20
1.5	0.30
2.0	0.40
3.0	0.60
4.0	0.80

Dilute each tube to 50 ml with ammonia-free water, add 1.0 ml of Nessler reagent and mix. After 20 minutes read the optical densities at 425 nm against the blank. From the values obtained plot optical density (absorbance) vs. concentration for the standard curve.

7.7.3 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

7.8 Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the optical density at 425 nm as described above for the Standards. Ammonia-nitrogen is read from the standard curve.

8. Calculation

8.1 If the titrimetric procedure is used calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{Total Kjeldahl nitrogen, mg/l} = \frac{(A-B) \times N \times F \times 1000}{S}$$

where:

A = milliliters of standard 0.020 N H_2SO_4 solution used in titrating sample.

B = milliliters of standard 0.020 N H_2SO_4 solution used in titrating blank.

N = normality of sulfuric acid solution

F = millequivalent weight of nitrogen (14 mg).

S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, mg/l} = \frac{(A-B) \times 280}{S}$$

8.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{A \times 1000}{0.8 \times S}$$

where:

A = mg NH_3N read from curve.

S = volume of distillate nesslerized.

8.3 Calculate Organic Kjeldahl Nitrogen in mg/l, as follows:

$$\text{Organic Kjeldahl Nitrogen} = \text{TKN} - NH_3N$$

9. Precision

9.1 Thirty-one analysts in twenty laboratory analyzed natural water samples containing exact increments of organic nitrogen, with the following results:

Increment as Nitrogen, Kjeldahl mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.20	0.197	+15.54	+.03
0.31	0.247	+ 5.45	+.02
4.10	1.056	+ 1.03	+.04
4.61	1.191	- 1.67	-.08

(FWPCA Method Study 2, Nutrient Analyses)

NITROGEN, KJELDAHL, TOTAL

(Automated Phenolate Method)

STORET NO. 00625

1. Scope and Application

1.1 This automated method may be used to determine Kjeldahl nitrogen in surface waters, domestic and industrial wastes, and saline waters. The applicable range is 0.05 to 2.0 mg N/l. Approximately 20 samples per hour can be analyzed.

2. Summary of Method

2.1 The sample is automatically digested with a sulfuric acid solution containing potassium sulfate and mercuric sulfate as a catalyst to convert organic nitrogen to ammonium sulfate. The solution is then automatically neutralized with sodium hydroxide solution and treated with alkaline phenol reagent and sodium hypochlorite reagent. This treatment forms a blue color designated as indophenol. Sodium nitroprusside, which increases the intensity of the color, is added to obtain necessary sensitivity for measurement of low level nitrogen.

3. Definitions

3.1 Total Kjeldahl nitrogen is defined as the sum of free ammonia and of organic compounds which are converted to $(NH_4)_2SO_4$ under the conditions of digestion which are specified below.

3.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free ammonia value from the total Kjeldahl nitrogen value. Also, organic Kjeldahl nitrogen may be determined directly by removal of ammonia before digestion.

4. Sample Handling and Preservation

4.1 Preservation by addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C is necessary.

5. Interferences

5.1 Iron and chromium ions tend to catalyze while copper ions tend to inhibit the indophenol color reaction.

6. Apparatus

6.1 Technicon AutoAnalyzer consisting of:

- 6.1.1 Sampler II, equipped with continuous mixer.
- 6.1.2 Two proportioning pumps.
- 6.1.3 Manifold I
- 6.1.4 Manifold II
- 6.1.5 Continuous Digester
- 6.1.6 Peristaltic pump
- 6.1.7 Five-gallon Carboy fume-trap
- 6.1.8 80°C Heating bath
- 6.1.9 Colorimeter equipped with 50 mm tubular flow cell and 630 nm filters.
- 6.1.10 Recorder equipped with range expander.

7. Reagents

7.1 Distilled Water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Furthermore, since organic contamination may interfere with this analysis, use of the resin Dowex XE-75 or equivalent which also tends to remove organic impurities is advised. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer.

7.2 Sulfuric acid: As it readily absorbs ammonia, special precaution must also be taken.with respect to its use. Do not store bottles reserved for this determination in areas of potential ammonia contamination.

7.3 EDTA (2% solution): Dissolve 20 g disodium ethylenediamine tetraacetate in 1 liter of distilled water. Adjust pH to 10.5-11.

7.4 Sodium hydroxide (30% solution): Dissolve 30°g NaOH in 1 liter of distilled water.

NOTE: The 30% sodium hydroxide should be sufficient to neutralize the digestate. In rare cases it may be necessary to increase the concentration of sodium hydroxide in this solution to insure neutralization of the digested sample in the manifold at the water jacketed mixing coil.

7.5 Sodium nitroprusside, Stock (1% solution): Dissolve 10 g $Na_2Fe(CN)_5$ $NO2H_2O$ in 1 liter distilled H_2O.

NOTE: This solution may be omitted if the nitrogen in the sample $\geq$ 0.1 mg/1.

7.6 Sodium nitroprusside, working solution: Dilute 50 ml stock solution to 1 liter with distilled water.

7.7 Alkaline phenol reagent: Pour 550 mls liquid phenol (88-90%) slowly with mixing and cooling into 1 liter of 40% NaOH. Make up to 2 liters with distilled water.

7.8 Sodium hypochlorite (1% solution): Dilute commercial "Clorox" - 200 ml to 1 liter with distilled water.

7.9 Digestion mixture: Place 2 g HgO in a 2-liter container. Slowly add, with stirring, 300 ml of acid water (100 ml H_2SO_4 - 200 ml H_2O) and stir until cool. Add 100 ml 10% K_2SO_4. Dilute to a volume of 2 liters with conc. sulfuric acid (approximately 500 ml at a time, allowing time for cooling).

7.10 Stock Solution: Dissolve 4.7619 g of pre-dried ammonium sulfate (1 hour at 105°C) in distilled water and dilute to 1.0 liter. Dissolve 2.1276 g of urea (desiccate only) in distilled water and dilute to 1.0 liter. Dissolve 10.5263 g of glutamic acid (desiccate only) in distilled water and dilute to 1.0 liter. 1 ml = 1.0 mg N.

7.11 Standard Solution: Dilute 10.0 ml of respective stock solution to 1.0 liter. 1 ml = 0.01 mg N.

7.10.1 Using the respective standard solutions, prepare the following standards in 100.0 ml volumetric flasks:

Conc., mg N/1	ml Standard Solution/100 ml
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.40	4.0
0.60	6.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

8. Procedure

8.1 Set up manifolds as shown in Figures 1, 2, and 3.

8.1.1 In the operation of Manifold No. 1, the control of three key factors is required to enable Manifold No. 2 to receive the mandatory representative feed. First, the digestive flowing into the pulse chamber (PC-1) must be bubble free, otherwise, air will accumulate in A-7, thus altering the ratio of sample to digestate in digestor. Second, in maintaining even flow from the helix. the peristaltic pump must be adjusted to cope with differences in density of the digestate and the wash water. Third, the sample pick-up rate from the helix must be precisely adjusted to insure that the entire sample is aspirated into the mixing chamber. And finally, the contents of the "Mixing Chamber" must be kept homogeneous by the proper adjustment of the air bubbling rate.

8.1.2 In the operation of Manifold No. 2, it is important in the neutralization of the digested sample to adjust the concentration of the NaOH so that the waste from the C-3 debubbler is slightly acid to Hydrion B paper.

8.1.3 The digester temperature is 390°C for the first stage and 360°C for the second and third stages.

8.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

8.3 Set sampling rate of Sampler II at 20 samples per hour, using a wash to sample ratio of 2 to 1 (1 minute sample, 2 minute wash).

NOTE: With a 2 minute sampling time plus two 2 minute washes, this actually represents 10 samples/hr.

8.4 Arrange various standards in Sampler cups in order of increasing concentration. Complete loading of sampler tray with unknown samples.

8.5 Switch sample line from distilled water to sampler and begin analysis.

8.5.1 If equipment is operating properly, 100% nitrogen recovery should be obtained for glutamic acid and urea when compared to ammonium sulfate standards.

9. Calculation

9.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

9.2 Any sample that has a computed concentration that is less than 10% of the sample run immediately prior to it must be rerun.

10. Precision and Accuracy

10.1 Six laboratories analyzed four natural water samples containing exact increments of organic nitrogen compounds, with the following results:

Increment as Kjeldahl-Nitrogen mg N/liter	Precision as Standard Deviation Kjeldahl-N, mg N/liter	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
1.89	0.54	-24.6	- .46
2.18	0.61	-28.3	- .62
5.09	1.25	-23.8	-1.21
5.81	1.85	-21.9	-1.27

(FWQA Method Study 4, Automated Methods - In preparation).

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1. Kammerer, P. A.; Rodel, M. G.; Hughes, R. A.; and Lee, G. F.; "Low Level Kjeldahl Nitrogen Determination on the Technicon AutoAnalyzer." Environmental Science and Technology. 1:4:340 (April 1967).
2. McDaniel, William H.; Hemphill, R. N.; Donaldson, W. T.; "Automatic Determination of Total Kjeldahl Nitrogen in Estuarine Waters." Presented at Technicon Symposium on Automation in Analytical Chemistry, New York, October 3, 1967.
3. B. O'Connor, Dobbs, Villiers, and Dean, "Laboratory Distillation of Municipal Waste Effluents". JWPCP 39, R 25, 1967.

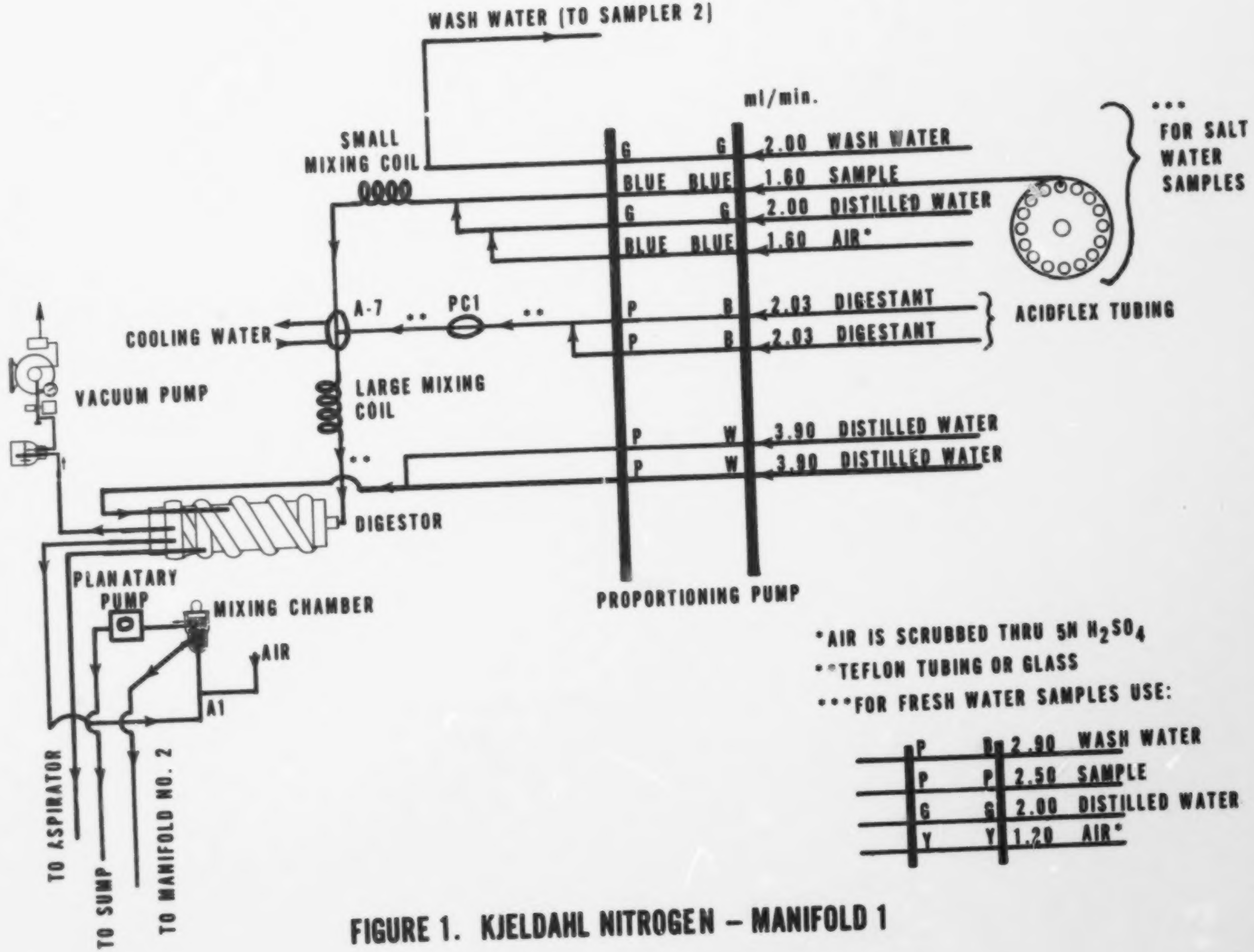
WASH WATER (TO SAMPLER 2)
ml/min.
SMALL MIXING COIL
G
G
2.00 WASH WATER
BLUE
BLUE
1.60 SAMPLE
G
G
2.00 DISTILLED WATER
BLUE
BLUE
1.60 AIR*
***
FOR SALT WATER SAMPLES
A-7
••
PC1
••
P
B
2.03 DIGESTANT
P
B
2.03 DIGESTANT
ACIDFLEX TUBING
COOLING WATER
VACUUM PUMP
LARGE MIXING COIL
P
W
3.90 DISTILLED WATER
P
W
3.90 DISTILLED WATER
••
DIGESTOR
PROPORTIONING PUMP
PLANATARY PUMP
MIXING CHAMBER
AIR
A1
P
B
2.90 WASH WATER
P
P
2.50 SAMPLE
G
G
2.00 DISTILLED WATER
Y
Y
1.20 AIR*
TO ASPIRATOR
TO SUMP
TO MANIFOLD NO. 2

FIGURE 1. KJELDAHL NITROGEN – MANIFOLD 1

*AIR IS SCRUBBED THRU 5N H_2SO_4

**TEFLON TUBING OR GLASS

***FOR FRESH WATER SAMPLES USE:

CONTINUOUS DIGESTER & MIXING CHAMBER ASSEMBLY

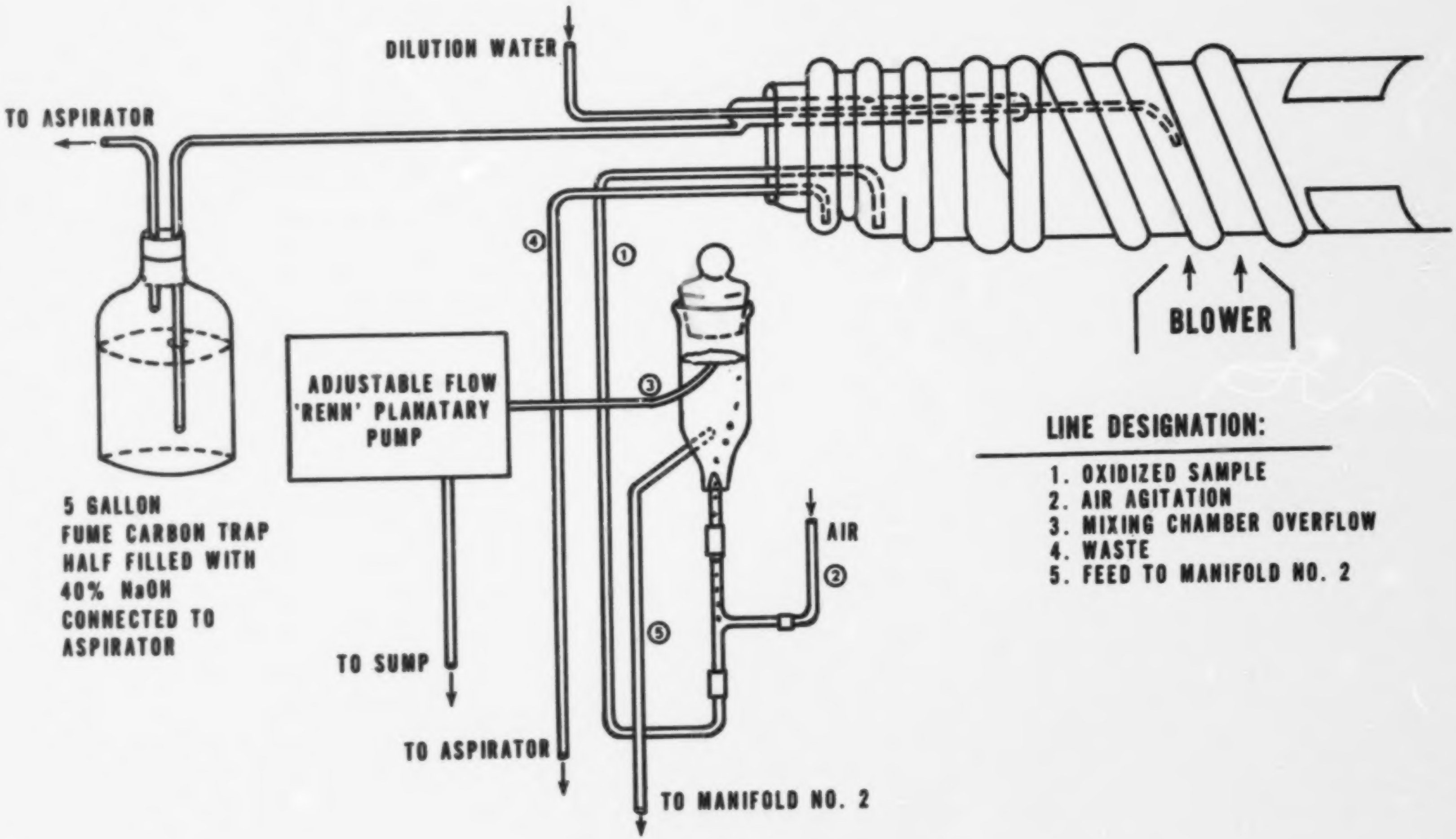
DILUTION WATER
TO ASPIRATOR
④
①
③
②
⑤
BLOWER
ADJUSTABLE FLOW 'RENN' PLANATARY PUMP
5 GALLON FUME CARBON TRAP HALF FILLED WITH 40% NaOH CONNECTED TO ASPIRATOR
TO SUMP
TO ASPIRATOR
AIR
TO MANIFOLD NO. 2
LINE DESIGNATION:
1. OXIDIZED SAMPLE
2. AIR AGITATION
3. MIXING CHAMBER OVERFLOW
4. WASTE
5. FEED TO MANIFOLD NO. 2

FIGURE 2. KJELDAHL NITROGEN

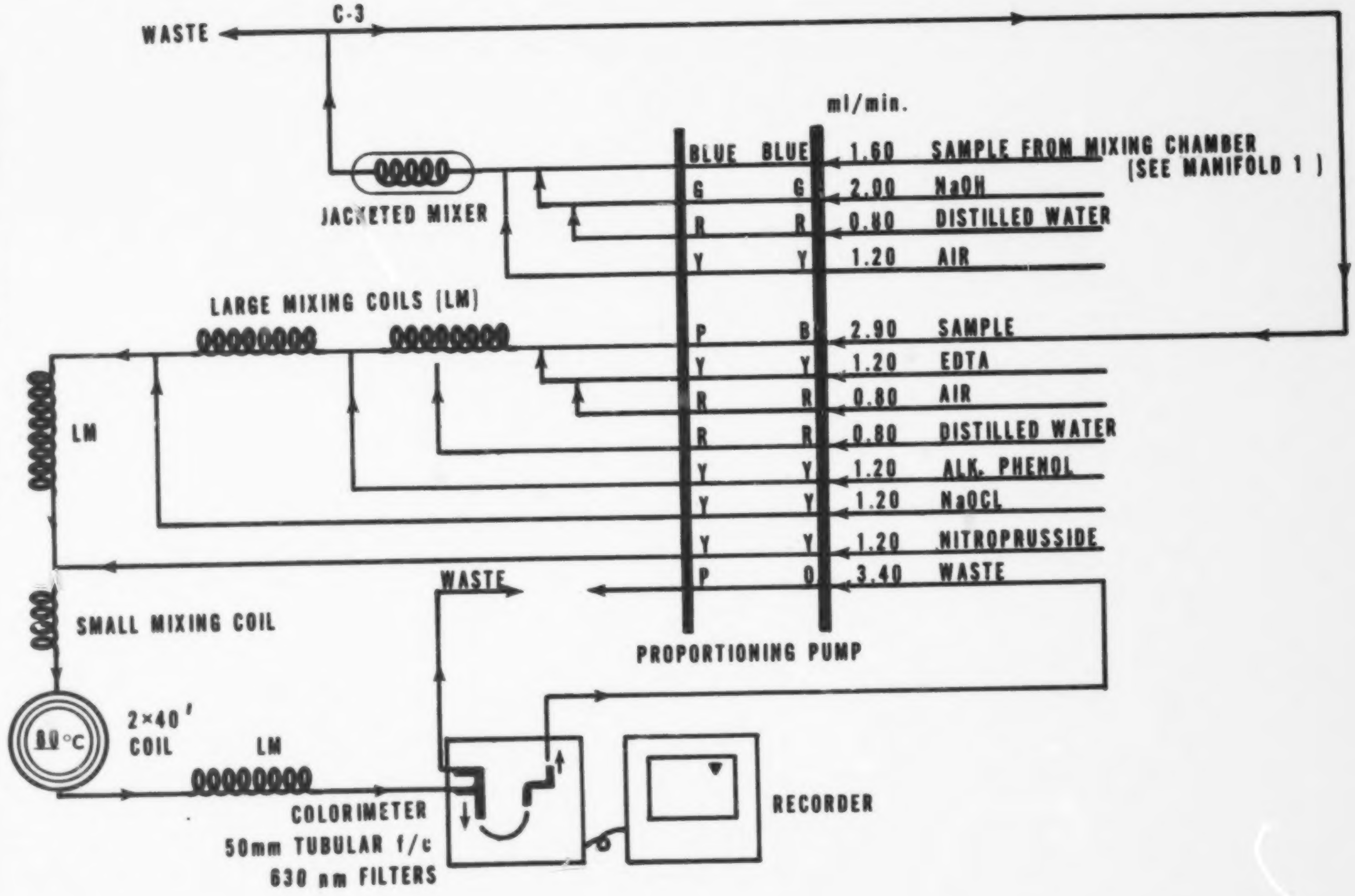
WASTE
C-3
ml/min.
BLUE
BLUE
1.60
SAMPLE FROM MIXING CHAMBER (SEE MANIFOLD 1)
G
G
2.00
NaOH
R
R
0.80
DISTILLED WATER
Y
Y
1.20
AIR
P
B
2.90
SAMPLE
Y
Y
1.20
EDTA
R
R
0.80
AIR
R
R
0.80
DISTILLED WATER
Y
Y
1.20
ALK. PHENOL
Y
Y
1.20
NaOCL
Y
Y
1.20
NITROPRUSSIDE
P
O
3.40
WASTE
PROPORTIONING PUMP
JACKETED MIXER
LARGE MIXING COILS (LM)
LM
SMALL MIXING COIL
80°C
2×40′ COIL
LM
WASTE
COLORIMETER
50mm TUBULAR f/c
630 nm FILTERS
RECORDER

FIGURE 3. KJELDAHL NITROGEN MANIFOLD 2.

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NITROGEN, NITRATE

STORET NO. 00620

1. Scope and Application

   1.1 This method is applicable to the analysis of surface waters, domestic and industrial wastes, and saline waters. Modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.

   1.2 The applicable range of concentrations is 0.1 to 2 mg NO_3N/liter.

2. Summary of Method

   2.1 This method is based upon the reaction of the nitrate ion with brucine sulfate in a 13 N H_2SO_4 solution at a temperature of 100°C. The color of the resulting complex is measured at 410 nm. Temperature control of the color reaction is extremely critical.

3. Sample Handling and Preservation

   3.1 Until more conclusive data is obtained, samples may be preserved by addition of 40 mg $HgCl_2$ per liter and storage at 4°C.

4. Interferences

   4.1 Dissolved organic matter will cause an off color in 13 N H_2SO_4 and must be compensated for by additions of all reagents except the brucine-sulfanilic acid reagent. This also applies to natural color present not due to dissolved organics.

   4.2 The effect of salinity is eliminated by addition of sodium chloride to the blanks, standards and samples.

   4.3 All strong oxidizing or reducing agents interfere. The presence of oxidizing agents may be determined by the addition of orthotolidine reagent.

   4.4 Residual chlorine interference is eliminated by the addition of sodium arsenite.

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4.5 Ferrous and ferric iron and quadrivalent manganese give slight positive interference, but in concentrations less than 1 mg/l these are negligible.

4.6 Uneven heating of the samples and standards during the reaction time will result in erratic values. The necessity for absolute control of temperature during the critical color development period cannot be too strongly emphasized.

5. Apparatus

5.1 Spectrophotometer or filter photometer suitable for measuring optical densities at 410 nm and capable of accommodating 25 mm diameter cells.

5.2 Sufficient number of 25 mm diameter matched tubes for reagent blanks, standards, and samples.

5.3 Neoprene coated wire racks to hold 25 mm diameter tubes.

5.4 Water bath suitable for use at 100°C. This bath should contain a stirring mechanism so that all tubes are at same temperature and should be of sufficient capacity to accept the required number of tubes without significant drop in temperature when the tubes are immersed.

5.5 Water bath suitable for use at 10-15°C.

6. Reagents

6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

6.2 Sodium chloride solution (300 g/l). Dissolve 300 g NaCl in distilled water and dilute to 1.0 l.

6.3 Sulfuric acid solution. Carefully add 500 ml H_2SO_4 (sp. gr. 1.84) to 125 ml distilled water. Cool and keep tightly stoppered to prevent absorption of atmospheric moisture.

6.4 Brucine-sulfanilic acid reagent. Dissolve 1 g brucine sulfate $[(C_{23}H_{26}N_2O_4)_2.H_2SO_4.7H_2O]$ and 0.1 g sulfanilic acid $(NH_2C_6H_4SO_3H.H_2O)$ in 70 ml hot distilled water. Add 3 ml concentrated HCl, cool, mix and dilute to 100 ml. Store in a dark bottle at 5°C. This solution is stable for several months; the pink color that develops slowly does not effect its usefulness. Mark bottle with warning: CAUTION: Brucine Sulfate is toxic; take care to avoid ingestion.

6.5 Potassium nitrate stock solution (1 ml = 0.1 mg NO_3-N). Dissolve 0.7218 g anhydrous potassium nitrate (KNO_3) in distilled water and dilute to 1 liter.

6.6 Potassium nitrate standard solution (1 ml = 0.001 mg NO_3-N). Dilute 10.0 ml of the stock solution to 1 liter. This standard solution should be prepared fresh weekly.

6.7 Acetic acid (1 + 3). Dilute 1 vol. glacial acetic acid (CH_3COOH) with 3 volumes of distilled water.

7. Procedure

7.1 Adjust the pH of the samples to approximately pH 7 with 1:3 acetic acid and, if necessary, filter through a 0.45µ pore size filter.

7.2 Set up the required number of matched tubes in the rack to handle reagent blank, standards and samples. It is suggested that tubes be spaced evenly throughout the rack to allow for even flow of bath water between the tubes. Even spacing of tubes should assist in achieving uniform heating of all tubes.

7.3 If it is necessary to correct for color or dissolved organic matter which will cause color on heating, a set of duplicate tubes must be used to which all reagents except the brucine-sulfanilic acid has been added.

7.4 Pipette 10.0 ml or an aliquot of the samples diluted to 10.0 ml into the sample tubes.

7.5 If the samples are saline, add 2 ml of the 30 percent sodium chloride solution to the reagent blank, standards and samples. For fresh water samples, sodium chloride solution may be omitted. Mix contents of tubes by swirling and place rack in cold water bath (0-10°C).

7.6 Pipette 10.0 ml of sulfuric acid solution into each tube and mix by swirling. Allow tubes to come to thermal equilibrium in the cold bath. Be sure that temperatures have equilibrated in all tubes before continuing.

7.7 Add 0.5 ml brucine-sulfanilic acid reagent to each tube (except the interference control tubes) and carefully mix by swirling, then place the rack of tubes in the boiling water bath for exactly 25 minutes. CAUTION: Immersion of the tube rack into the bath should not decrease the temperature of the bath more than 1 to 2°C. Flow of bath water between the tubes should not be restricted by crowding too many tubes into the rack, in order to keep this temperature decrease to an absolute minimum. If color development in the standards reveals discrepancies in the procedure the operator should repeat the procedure after reviewing the temperature control steps.

7.8 Remove rack of tubes from the hot water bath and immerse in the cold water bath and allow to reach thermal equilibrium (20-25°C).

7.9 Dry tubes and read optical density against the reagent blank at 410 nm.

8. Calculation

8.1 Obtain a standard curve by plotting the optical densities of standards run by the above procedure against mg NO_3-N. (The color reaction does not always follow Beer's law).

8.2 Subtract the absorbance of the sample without the brucine-sulfanilic reagent from the absorbance of the sample containing brucine-sulfanilic acid and read the optical density in mg NO_3-N. Multiply by factor for converting mg per aliquot of sample to mg per liter.

9. Precision and Accuracy

9.1 Twenty-seven analysts in fifteen laboratories analyzed natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrogen, Nitrate mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.16	.092	-6.79	-.01
0.19	.083	+8.30	+.02
1.08	.245	+4.12	+.04
1.24	.214	+2.82	+.04

(FWPCA Method Study 2, Nutrient Analyses).

NITROGEN, NITRATE-NITRITE

(Automated Cadmium Reduction Method)

STORET NO. 00620

1. Scope and Application

1.1 This method pertains to the determination of nitrates and nitrites, singly or combined, present in surface and saline waters. The prescribed specifications permit analyses of samples in the range of 0.05 to 10 mg/liter, N present as NO_3.

2. Summary of Method(1)

2.1 The initial step(2) is to reduce the nitrates to nitrites by using a cadmium-copper catalyst. The nitrites (those originally present plus reduced nitrates) are then reacted with sulfanilamide to form the diazo compound which is then coupled in an acid solution (pH 2.0 - 2.5) with N-1 naphthyl-ethylenediamine hydrochloride to form the azo dye. The azo dye intensity, which is proportional to the nitrate concentration, is then measured. Separate rather than combined nitrate-nitrite values are readily obtainable by carrying out the procedure--first with, and then without, the initial Cd-Cu reduction step.

3. Sample Handling and Preservation

3.1 Preservation by addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C is necessary.

4. Interferences

4.1 Ammonia and primary amines which are frequently present in natural waters may react to some extent with nitrites to form nitrogen. Thus, since, as in nature, the sample is not stable, the analyses should be performed as soon as possible.

4.2 In surface waters normally encountered in surveillance studies, the concentration of oxidizing or reducing agents and potentially interfering metal ions are well below the limits causing interferences. When present in sufficient concentration, metal ions may produce a positive error, i.e., Hg (II) and Cu (II), may form colored complex ions having absorption bands in the region of color measurement.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of the following components:

5.1.1 Sampler II.

5.1.2 Manifold (including Cu-Cd column).

5.1.3 Colorimeter equipped with 50 mm tubular flow cell and 540 nm filters.

5.1.4 Range expander.

5.1.5 Recorder.

5.2 Cadmium-copper reduction column$^{(2)}$.

5.2.1 Preparation: Shake the 30 - 60 mesh av. diam. 0.5 mm cadmium turnings with a solution of 2% (wt/vol) copper sulfate pentahydrate solution. A weight of solution equal to 10 times the weight of the cadmium is used. The copper sulfate-treated cadmium catalyst is then placed in a 8 mm x 50 mm pyrex tubing and is followed by copper granules (0.6 mm x 3.0 mm) made from hydrogen treated copper wire (Note 1). The volume ratio of the cadmium bed to that of the copper should be about 3 - 1 to 4 - 1. (See Figure 1). Pyrex wool, inserted at the lower end of the reactor, is used to prevent the catalyst from dropping out of the reactor. The ends of the reactor are fabricated to accomodate the reactor into the system. The sample enters the column at the copper granule-packed end. To minimize back pressure due to a vertical position or channelling due to a horizontal position, the reductant tube is placed in an up-flow 20° incline.

Note 1 - Supplied by F&M Scientific Corp., Avondale, Pa.

5.2.2 Regeneration: HCl, diluted 1 to 4, is pumped through the NH_4Cl line for one minute, followed by water for two minutes and then 2% copper sulfate solution for five minutes. For complete cleaning and coating, remove the column from the manifold. Using a small funnel and a short plastic connecting tube, the acid water and copper sulfate solution are successively poured into the column and allowed to flow through by gravity. The cadmium should ultimately acquire a moss-black appearance and the copper, a bright orange.

6. Reagents

6.1 Distilled water: Because of possible contamination, this should be prepared by passage through an ion exchange column comprised of a mixture of both strongly acidic-cation and strongly basic-anion exchange resins. The regeneration of the ion exchange column should be carried out according to the manufacturer's instructions.

6.2 Color reagent: To approximately 800 ml of distilled water, add, while stirring, 100 ml concentrated phosphoric acid, 40 g sulfanilamide, and 2 g N-1 naphthylethylenediamine dihydrochloride. Stir until dissolved and dilute to one liter. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.

6.3 Wash solution: Use distilled water for unpreserved samples; samples preserved with H_2SO_4, use 1 ml H_2SO_4 per liter of wash water.

6.4 Ammonium Chloride Solution (8.5% NH_4Cl): Dissolve 85 g of reagent grade ammonium chloride in distilled water and dilute to one liter with distilled water. Add 1/2 ml Brij-35(4).

6.5 Stock nitrate solution: Dissolve 7.218 g KNO_3 and dilute to 1.0 l with distilled water. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months. 1 ml = 1.0 mg NO_3-N.

6.6 Stock nitrite solution: Dissolve 6.072 g KNO_2 and dilute to 1.0 l with distilled water. Solution is unstable; prepare as required. 1 ml = 1.0 mg NO_2-N.

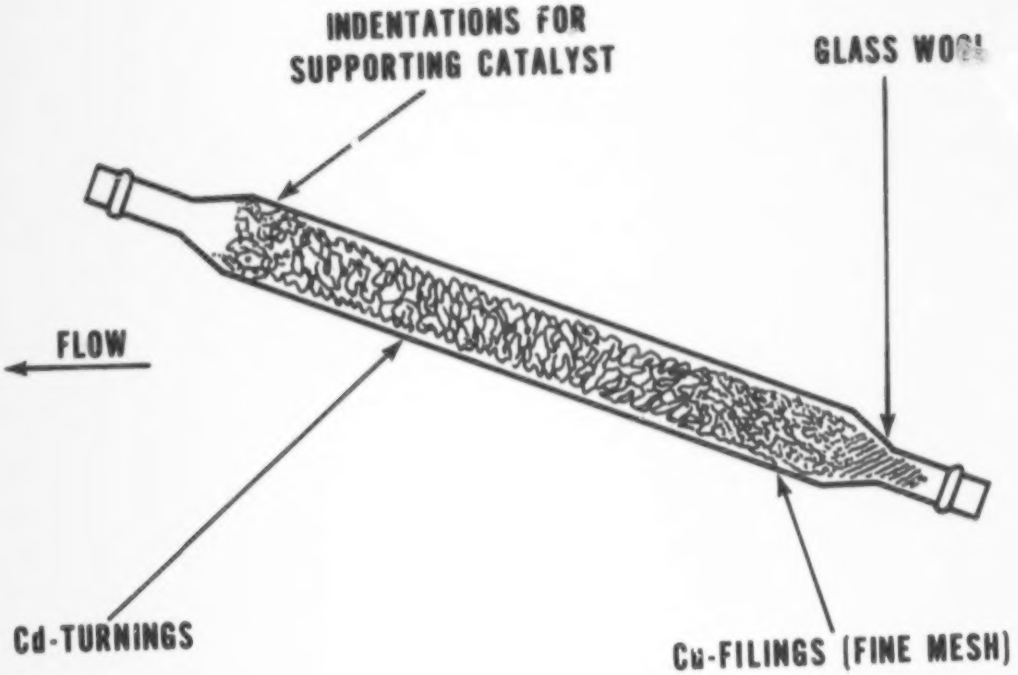
6.7 Standard nitrate solution: Dilute 10.0 ml of stock nitrate solution to 1 liter. 1 ml = 0.01 mg NO_3-N. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months.

6.8 Standard nitrite solution: Dilute 10.0 ml of stock nitrite solution to 1 liter. 1 ml = 0.01 mg NO_2-N. Solution is unstable; prepare as required.

6.9 Using either standard nitrate solution or standard nitrite solution, prepare the following standards in 100.0 ml volumetric flasks:

Conc., mg NO_3-N or NO_2-N/l	Standard Solution/100 ml
0.0	0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0
2.00	20.0
4.00	40.0
6.00	60.0

Note: When the samples to be analyzed are saline waters, substitute Ocean Water (SOW) (5) should be used for preparing the standards;


INDENTATIONS FOR SUPPORTING CATALYST
GLASS WOOL
FLOW
Cd-TURNINGS
Cu-FILINGS (FINE MESH)

TILT COLUMN TO 20° POSTION

FIGURE 1. CADMIUM-COPPER REDUCTION COLUMN
(1 1/2 ACTUAL SIZE)

otherwise, distilled water is used. A tabulation of SOW composition follows:

$NaCl$ - 24.53 g/l $MgCl_2$ - 5.20 g/l Na_2SO_4 - 4.09 g/l
$CaCl_2$ - 1.16 g/l KCl - 0.70 g/l $NaHCO_3$ - 0.20 g/l
KBr - 0.10 g/l H_3BO_3 - 0.03 g/l $SrCl_2$ - 0.03 g/l
NaF - 0.003 g/l

7. Procedure

7.1 Set up the manifold as shown in Figure 2. Note that reductant column should be in 20° incline position with Cu at lower end.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.3 Place appropriate nitrate and/or nitrite standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.4 Switch sample line to sampler and start analysis.

8. Calculations

8.1 Prepare appropriate standard curve or curves derived from processing NO_3 and/or NO_2 standard through manifold. Compute concentration of samples by comparing sample peak heights with standard curve. Any sample whose computed concentration is less than 10% of its immediate predecessor must be rerun.

9. Precision and Accuracy

9.1 Three laboratories analyzed four natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrate Nitrogen mg N/Liter	Precision as Standard Deviation mg N/liter	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
0.29	0.012	+ 5.75	+.017
0.35	0.092	+18.10	+.063
2.31	0.318	+ 4.47	+.103
2.48	0.176	- 2.69	-.067

(FWQA Method Study 4, Automated Methods - In preparation)

References

1. J. E. O'Brien and J. Fiore, "Automation in Sanitary Chemistry - parts 1 & 2 Determination of Nitrates and Nitrites." Wastes Engineering, 33, 128 & 238 (1962).
2. J. D. Strickland, C. R. Stearns, and F. A. Armstrong, "The Measurement of Upwelling and Subsequent Biological Processes by Means of the Technicon AutoAnalyzer and Associated Equipment." Deep Sea Research 14, 381-389 (1967).
3. "ASTM Manual on Industrial Water and Industrial Waste Water," Method D 1254, page 465 (1966).
4. Chemical Analyses for Water Quality Manual, Department of the Interior, FWPCA, R. A. Taft Sanitary Engineering Center Training Program, Cincinnati, Ohio 45226 (January 1966).
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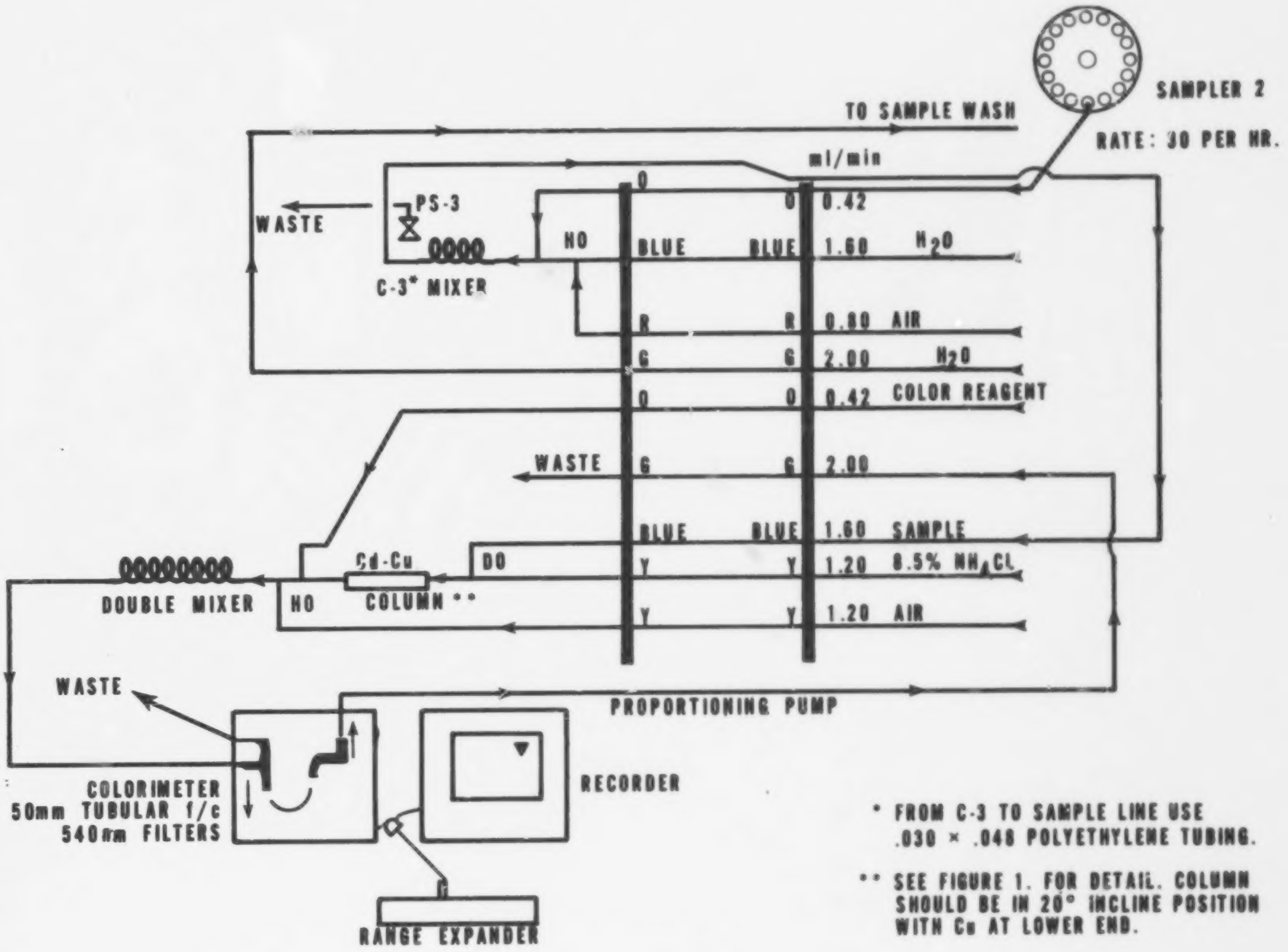
SAMPLER 2
RATE: 30 PER HR.
TO SAMPLE WASH
ml/min
WASTE
PS-3
C-3* MIXER
HO
O
BLUE
R
G
O
G
BLUE
Y
Y
O 0.42
BLUE 1.60 H2O
R 0.80 AIR
G 2.00 H2O
O 0.42 COLOR REAGENT
G 2.00
BLUE 1.60 SAMPLE
Y 1.20 8.5% NH4CL
Y 1.20 AIR
WASTE
DO
Cd-Cu
COLUMN **
HO
DOUBLE MIXER
WASTE
PROPORTIONING PUMP
COLORIMETER
50mm TUBULAR f/c
540nm FILTERS
RECORDER
RANGE EXPANDER

* FROM C-3 TO SAMPLE LINE USE .030 × .048 POLYETHYLENE TUBING.

** SEE FIGURE 1. FOR DETAIL. COLUMN SHOULD BE IN 20° INCLINE POSITION WITH Cu AT LOWER END.

FIGURE 2. NITRATE-NITRITE MANIFOLD

NITROGEN, NITRATE AND NITRITE

(Automated Hydrazine Reduction Method)

STORET NO. 00620

1. Scope and Application

1.1 This method is applicable to surface waters, and domestic and industrial wastes which contain less than 500 mg/l calcium. The applicable range of this method is 0.05-10 mg/l nitrite or nitrate nitrogen. Approximately 20 samples per hour can be analyzed.

2. Summary of Method

2.1 This method, using the Technicon AutoAnalyzer, determines NO_2-N by the conventional diazotization-coupling reaction. The NO_3-N is reduced with hydrazine sulfate in another portion of the sample and the nitrite thus formed is determined in the usual manner.

2.2 Subtraction of the NO_2-N originally present in the sample from the total NO_2-N found will give the original NO_3-N concentration in terms of NO_2-N.

3. Sample Handling and Preservation

3.1 Preservation by addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C.

4. Interferences

4.1 The following table lists the concentration of ions that cause no interference in the determination of nitrite and nitrate nitrogen. The same interfering ion concentration applies to either nitrite or nitrate:

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Ion	mg/l Ion Not Causing Interference
Cl^-	30,000
PO_4^{-3}	50
S^{-2}	Note
NH_3-N	80
Mg^{+2}	75
Ca^{+2}	240
Fe^{+3}	30
ABS	60

Note 1. -- The apparent NO_3 and NO_2 concentrations varied ±10 percent with concentrations of sulfide ion up to 10 mg/l.

4.2 The pH of the samples should be between 6 and 9.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Two proportional pumps.

5.1.2 Two colorimeters each with an 8 mm flow-through cell and 520 nm filters.

5.1.3 One continuous filter.

5.1.4 One Sampler I.

5.1.5 Two recorders.

5.1.6 One 38°C temperature bath.

5.1.7 Two time delay coils.

6. Reagents

6.1 Color developing reagent: To approximately 3 liters of distilled water add 400 ml concentrated phosphoric acid (sp. gr. 1.834), 60 g sulfanilamide ($H_2H-C_6H_4SO_2NH_2$) followed by 3.0 g N (1-Naphthyl) ethylene-diamine dihydrochloride. Dilute the solution to 4 liters with distilled water and store in a dark bottle in the refrigerator. This solution is stable for approximately 1 month.

NOTE 2: It may be necessary to apply heat in order to dissolve the sulfanilamide.

6.2 Copper sulfate; stock solution: Dissolve 2.5 g of copper sulfate ($CuSO_4.5H_2O$) in distilled water and dilute to 1 liter.

6.3 Copper sulfate; dilute solution: Dilute 20 ml of stock solution to 2 liters with distilled water.

6.4 Sodium hydroxide; stock solution, (10 N): Dissolve 400 g NaOH in 750 ml distilled water, cool and dilute to 1 liter.

6.5 Sodium hydroxide (1.0N): Dilute 100 ml of stock NaOH solution to 1 liter.

6.6 Sodium hydroxide (0.3N): Dilute 60 ml of stock NaOH to 2 liters.

6.7 Hydrazine sulfate; stock solution: Dissolve 54.92 g of hydrazine sulfate ($N_2H_4.H_2SO_4$) in 1800 ml of distilled water and dilute to 2.0 1. This solution is stable for approximately 6 months.

CAUTION: Toxic if ingested. Mark container with warning.

6.8 Hydrazine sulfate; dilute solution: Dilute 90 ml of stock solution to 4 liters with distilled water to obtain working solution. Make up fresh daily.

6.9 Potassium nitrate; stock solution (1000 mg/1 . NO_3-N): Dissolve 7.2180 g of KNO_3, oven dried at 100-105°C for 2 hours, in distilled water and dilute to 1.0 1. Add 1 ml chloroform as a preservative. Stable for 6 months.

6.10 Potassium nitrate; standard solution (100 mg/l NO_3-N): Dilute 50 ml of stock KNO_3 solution to 500 ml in a volumetric flask. From this dilute solution prepare the following standards in 500 ml volumetric flasks:

mg/l NO_3-N	ml Standard Solution
0.4	2.0
1.0	5.0
1.6	8.0
3.0	15.0
5.0	25.0
7.0	35.0
10.0	50.0

6.11 Sodium nitrite; stock solution (1000 mg/l NO_2-N): Dissolve 4.9260 g $NaNO_2$, oven dried at 100-105°C for two hours, in distilled water and dilute to 1.0 l. Add 1 ml chloroform as preservative. Store in the refrigerator. Stable for 1 month.

6.12 Sodium nitrite; standard solution (100 mg/l): Dilute 50 ml of stock $NaNO_2$ solution to 500 ml in a volumetric flask. From this dilute solution prepare the same volumetric standards as in 6.9. Prepare fresh each week.

7. Procedure

7.1 Set up the manifold as shown in Figures 1 and 2. Allow both colorimeter (with the proper filters) and recorder to warm up for 30 minutes, then run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on each colorimeter. Adjust baseline to 0.01 optical density. Place a distilled water wash tube in alternate openings on sampler and set sample timing at 1.5 minutes.

7.2 Run a 2.0 mg/l NO_3-N and a 2.0 mg/l NO_2-N standard through the system to check for 100% reduction of nitrate to nitrite. The two peaks should be of equal height. If the NO_3 peak is lower than that of the NO_2 peak, the temperature of the reduction bath should be increased until they are equal. If the NO_3 peak is higher than the nitrate, the temperature should be reduced. When the correct temperature of the bath has been determined, no further adjustment should be necessary.

7.3 Arrange standards in sampler in NO_2-NO_3 order with increasing concentration of nitrogen. Place unknown samples in sampler tubes and place in alternate openings of sampler. A NO_2 and NO_3 standard of equal nitrogen concentration should be placed after every 10 samples as a further check on the system and to more easily identify peaks.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentrations of samples by comparing sample peak heights with standard curve.

8.2 Subtract the NO_2 concentration in the sample from the total NO_2 found (nitrite plus nitrate) on the reduction side to calculate the NO_3 concentration in the sample.

9. Precision and Accuracy

9.1 Nine laboratories analyzed four natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrate Nitrogen mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.29	0.053	-0.8	.002
0.35	0.058	+1.9	.007
2.31	0.258	+3.0	.07
2.48	0.217	-1.2	.03

(FWQA Method Study 4, Automated Method - In preparation).

9.2 In a single laboratory (AQC), using surface water samples at concentrations of 0.1, 0.2, 0.8, and 2.1 mg-N/1, the standard deviations were 0.0, ±0.04, ±0.05, and ±0.05, respectively.

9.3 In a single laboratory (AQC), using surface water samples at concentrations of 0.2 and 2.2 mg N/1, recoveries were 100% and 96%, respectively.

References

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2. L. Kamphake, S. Hannah, and J. Cohen, "Automated Analysis for Nitrate by Hydrazine Reduction." Water Research, 1, 205 (1967).

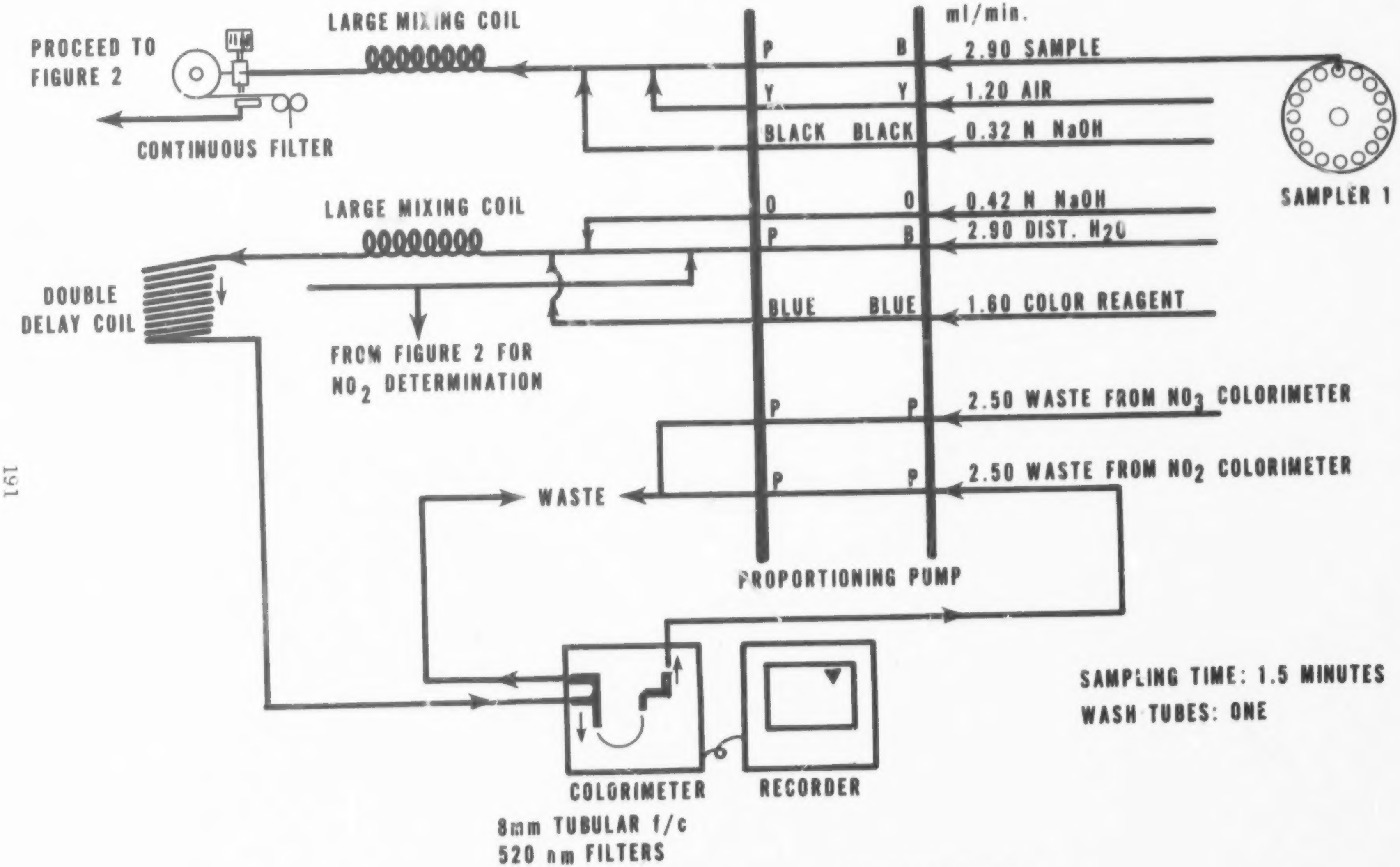
ml/min.
PROCEED TO FIGURE 2
LARGE MIXING COIL
CONTINUOUS FILTER
P
B
2.90 SAMPLE
Y
Y
1.20 AIR
BLACK
BLACK
0.32 N NaOH
SAMPLER 1
LARGE MIXING COIL
O
O
0.42 N NaOH
P
B
2.90 DIST. H2O
DOUBLE DELAY COIL
BLUE
BLUE
1.60 COLOR REAGENT
FROM FIGURE 2 FOR NO2 DETERMINATION
P
P
2.50 WASTE FROM NO3 COLORIMETER
P
P
2.50 WASTE FROM NO2 COLORIMETER
WASTE
PROPORTIONING PUMP
SAMPLING TIME: 1.5 MINUTES
WASH TUBES: ONE
COLORIMETER
RECORDER
8mm TUBULAR f/c
520 nm FILTERS

FIGURE 1. NITRATE-NITRITE MANIFOLD

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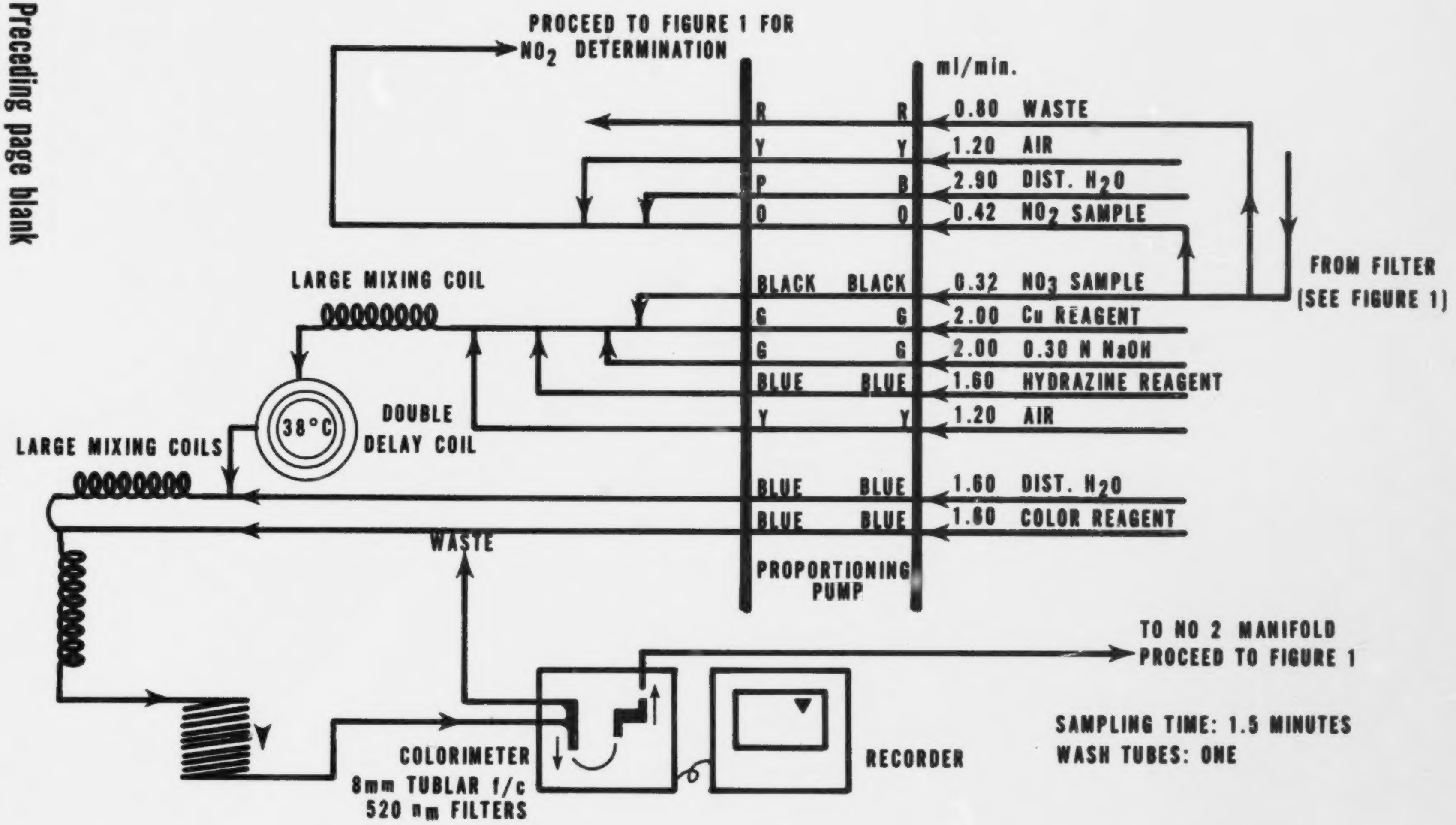
PROCEED TO FIGURE 1 FOR
NO_2 DETERMINATION
ml/min.
R R 0.80 WASTE
Y Y 1.20 AIR
P B 2.90 DIST. H_2O
O O 0.42 NO_2 SAMPLE
BLACK BLACK 0.32 NO_3 SAMPLE
G G 2.00 Cu REAGENT
G G 2.00 0.30 N NaOH
BLUE BLUE 1.60 HYDRAZINE REAGENT
Y Y 1.20 AIR
BLUE BLUE 1.60 DIST. H_2O
BLUE BLUE 1.60 COLOR REAGENT
FROM FILTER
(SEE FIGURE 1)
LARGE MIXING COIL
38°C
DOUBLE
DELAY COIL
LARGE MIXING COILS
WASTE
PROPORTIONING
PUMP
TO NO 2 MANIFOLD
PROCEED TO FIGURE 1
COLORIMETER
8mm TUBLAR f/c
520 nm FILTERS
RECORDER
SAMPLING TIME: 1.5 MINUTES
WASH TUBES: ONE

FIGURE 2. NITRATE-NITRITE MANIFOLD

NITROGEN, NITRITE

STORET NO. 00615

1. Scope and Application

1.1 This method is applicable to the determination of nitrite in surface waters, domestic and industrial wastes and saline waters.

1.2 The method is applicable in the range from 0.05 to 1.0 mg/l NO_2/N.

2. Summary of Method

2.1 The diazonium compound formed by diazotation of sulfanilamide by nitrite in water under acid conditions is coupled with N-(1-naphthyl)-ethylenediamine to produce a reddish-purple color which is read in a spectrophotometer at 540 nm.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples may be preserved by addition of 40 mg $HgCl_2$ per liter and stored at 4°C.

4. Interferences

4.1 There are very few known interferences at concentrations less than 1,000 times that of the nitrite; however, recent addition of strong oxidants or reductants to the samples will readily affect the nitrite concentrations. High alkalinity (>600 mg/l) will give low results due to a shift in pH of the color reaction.

5. Apparatus

5.1 Spectrophotometer equipped with 1.0 and 5.0 cm cuvettes for use at 540 nm.

5.2 Nessler tubes, 50 ml or volumetric flasks, 50 ml.

6. Reagents

6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

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6.2 Buffer-color reagent. To 250 ml of distilled water, add 105 ml concentrated hydrochloric acid, 5.0 g sulfanilamide and 0.5 g N-(1-Naphthyl) ethylenediamine dihydrochloride. Stir until dissolved. Add 136 g of sodium acetate and again stir until dissolved. Dilute to 500 ml with distilled water. This solution is stable for several weeks if stored in the dark.

6.3 Nitrite-nitrogen stock solution, 1.0 ml = 0.10 mg NO_2-N. Dissolve 0.4926 g of dried anhydrous sodium nitrite (24 hours in desiccator) in distilled water and dilute to 1.0 l. Preserve with 2 ml chloroform per liter.

6.4 Nitrite-nitrogen standard solution, 1.0 ml = 0.001 mg NO_2-N. Dilute 10 ml of the stock solution to 1.0 liter.

7. Procedure

7.1 If the sample has a pH greater than 10 or a total alkalinity in excess of 600 mg/l, adjust to approximately pH 6 with 1:3 HCl.

7.2 Filter the sample through a 0.45 µ pore size filter using the first portion of filtrate to rinse the filter flask.

7.3 Place 50 ml of sample, or an aliquot diluted to 50 ml, in a 50 ml Nessler tube; hold until preparation of standards is completed.

7.4 At the same time prepare a series of standards in 50 ml Nessler tubes as follows:

ml of Standard Solution 1.0 ml = 0.001 mg NO_2-N	Conc., When Diluted to 50 ml, mg/l of NO_2-N
0.0 (Blank)	0.0
0.5	0.01
1.0	0.02
1.5	0.03
2.0	0.04
3.0	0.06
4.0	0.08
5.0	0.10
10.0	0.20

7.5 Add 2.0 ml of buffer-colored reagent to each standard and sample, mix and allow color to develop for at least 15 minutes. The color reaction medium should be between pH 1.5 and 2.0.

7.6 Read the color in the spectrophotometer at 540 nm against the blank and plot concentration of NO_2-N against optical density.

8. Calculation

8.1 Read the concentration of NO_2-N directly from the curve.

8.2 Calculate the concentration of NO_2-N in the sample in milligrams per liter as follows:

$$NO_2\text{-N, mg/l} = \frac{\text{absorbance of sample x mg/l standard x 50}}{\text{absorbance of standard x ml sample}}$$

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

NITROGEN, ORGANIC + AMMONIA

(Automated Phenolate Method)

STORET NO. 00635

1. Scope and Application

   1.1 This automated method is applicable to surface and saline waters. The applicable range is 1.0 to 10.0 mg N/l. Approximately 15 samples per hour can be analyzed.

2. Summary of Method

   2.1 Organic nitrogen is determined by manually digesting the sample with potassium persulfate and sulfuric acid to convert the organic nitrogen, and any ammonia present, to ammonium sulfate. Subsequently, the automated phenol-hypochlorite procedure is used to measure the ammonia nitrogen. Nitrate-nitrite nitrogen is not measured by this procedure.

3. Sample Handling and Preservation

   3.1 Preservation by addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C is necessary.

4. Interferences

   4.1 No significant interferences.

5. Apparatus

   5.1 Technicon AutoAnalyzer consisting of:

      5.1.1 Sampler I.

      5.1.2 Continuous Filter.

      5.1.3 Manifold.

      5.1.4 Proportioning Pump.

      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 650 nm filters.

      5.1.6 Recorder equipped with range expander.

   5.2 Hot plate.

6. Reagents

6.1 Distilled Water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. Since organic contaminants may interfere with this analysis, use of the resin Dowex XE-75 or equivalent which also tends to remove organic impurities is advised. The regeneration of the ion exchange column should be carried out according to the instructions of the manufacturer.

Note: All glassware must be pre-rinsed with this ammonia-free water to prevent contamination.

6.2 Sulfuric Acid: As it readily absorbs ammonia, special precaution must also be taken with respect to its use. Do not store bottles reserved for this determination in areas of potential ammonia contamination.

6.3 Potassium persulfate, low N (0.001%): Certain lots of this reagent do not meet this specification for nitrogen content. In order to insure this purity, dissolve 50 g of the reagent in 500 ml of distilled water at 60° to 70°C. Make alkaline with 10 ml of sodium hydroxide solution, 2.2M. Bubble air that has been passed through a 10% sulfuric acid solution through a tube which has been drawn into a capillary into the solution while withdrawing air from the solution, which is contained in a suction flask, under reduced pressure. Control the air flow so that a rather vigorous bubbling through the solution is maintained. After 30 minutes of vigorous bubbling, cool the solution overnight in a refrigerator at about 4°C. Filter the crop of crystals through a No. 40

Whatman filter paper previously washed with ammonia-free water. Wash the crystals with ice-cold ammonia-free water. Dry the crystals at 60 to 70°C and store in a tightly closed reagent bottle.

6.4 Sulfuric acid solution: Add slowly and with stirring 310 ml of reagent grade, concentrated sulfuric acid to 600 ml of ammonia-free water. Cool and dilute to 1.0 l.

6.5 Phenol solution: Dissolve 83 g of phenol in 500 ml of ammonia-free water by stirring with a Teflon coated magnet for 10 minutes. Add 32 g NaOH and dilute to 1 liter.

6.6 Sodium hypochlorite solution: Dilute 250 ml of bleach solution containing a 5.25% NaOCl to 500 ml with ammonia-free water.

6.7 Neutralizing solution: Dissolve 6 g EDTA disodium salt and 65 g of NaOH in 500 ml of distilled water. Dilute to 1.0 l.

6.8 Stock solution: Dissolve 4.7168 g of ammonium sulfate analytical reagent in ammonia-free water and dilute to 1.0 l. 1.0 ml = 1.00 mg N.

6.9 Standard solution: Dilute 10.0 ml of stock solution to 100.0 ml. 1 ml = 0.10 mg N.

6.9.1 Using standard solution, prepare the following standards in 100-ml volumetric flasks:

mg N/l	ml Standard Solution/100 ml
0.0	0
1.0	1.0
2.0	2.0
3.0	3.0
4.0	4.0
5.0	5.0
6.0	6.0
8.0	8.0
10.0	10.0

Note: Standards should be processed through complete procedure in same manner as samples.

7. Procedure

7.1 Transfer a 25 ml sample of water to a 125 ml Erlenmeyer flask.

7.2 Add 3 ml of sulfuric acid solution and evaporate on a hot plate to light fumes of SO_3. This step may require approximately one hour. Close attention is not required of the sample; however, it should not be allowed to go to dryness. Cool the sample.

7.3 Add 1 ml of ammonia-free water and 1 g of potassium persulfate, low N, and swirl the flask.

7.4 Digest the sample on the hot plate for 15 minutes. Fumes of SO_3 should begin coming off after 7 minutes. The samples should become clear and transparent after this step, except in the presence of large amounts of silica. Cool the sample; dilute to 25 ml with ammonia-free water. The sample is now ready for automatic analysis.

7.5 Set up manifold as shown in Figure 1.

7.6 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.7 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.0 minutes.

7.8 Arrange standards in Sampler in order of decreasing concentration. Complete loading of Sampler tray with unknown samples from 7.4.

7.9 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

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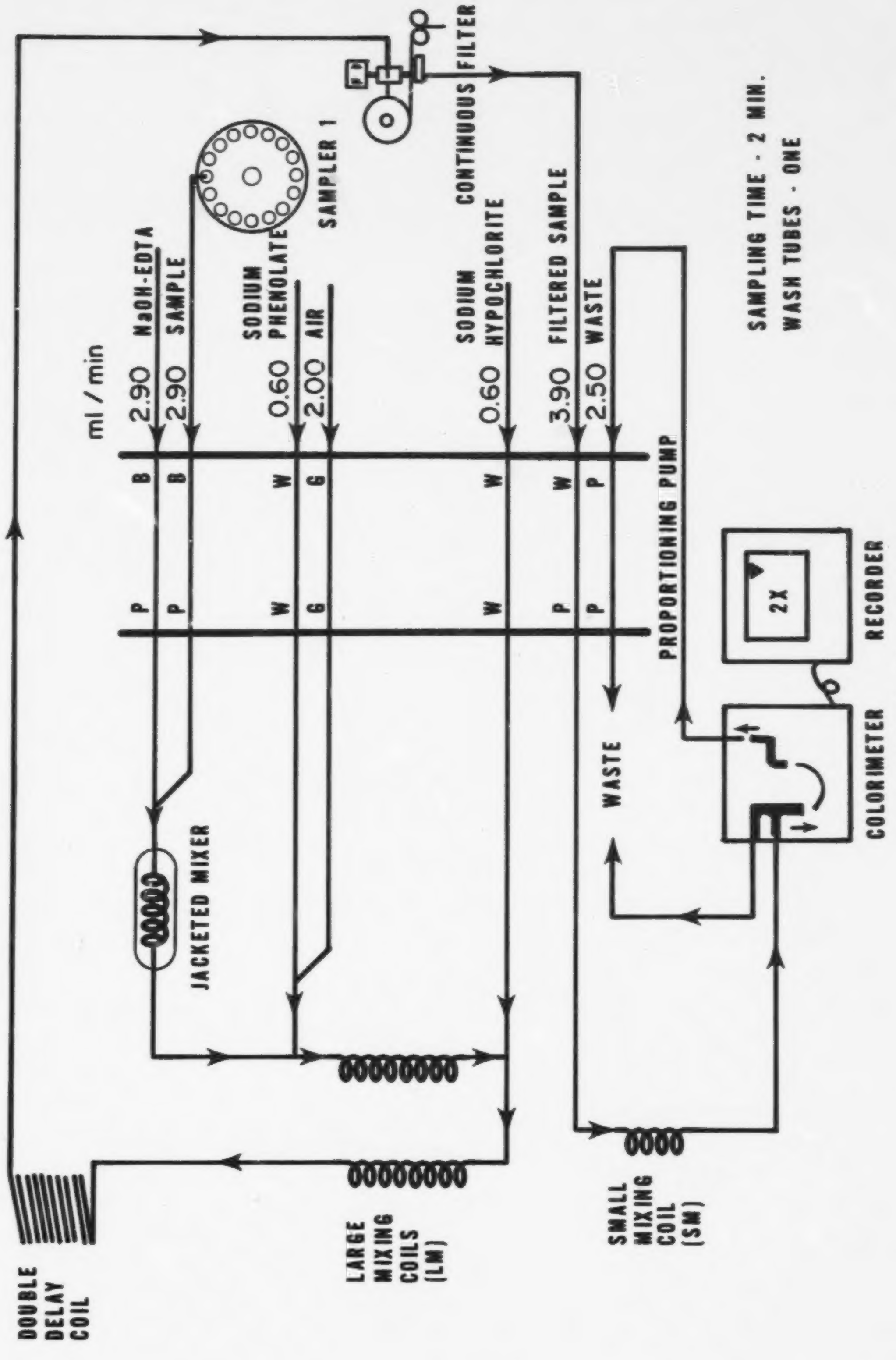
ml / min
2.90 NaOH-EDTA
2.90 SAMPLE
0.60 SODIUM PHENOLATE
2.00 AIR
0.60 SODIUM HYPOCHLORITE
3.90 FILTERED SAMPLE
2.50 WASTE
B P
B P
W W
G G
W W
W P
P P
SAMPLER 1
CONTINUOUS FILTER
PROPORTIONING PUMP
JACKETED MIXER
WASTE
COLORIMETER
15mm TUBULAR f/c
650 nm FILTERS
RECORDER
2X
DOUBLE DELAY COIL
LARGE MIXING COILS (LM)
SMALL MIXING COIL (SM)

SAMPLING TIME - 2 MIN.
WASH TUBES - ONE

FIGURE 1 - ORGANIC NITROGEN & AMMONIA MANIFOLD

NTA

(Zinc-Zincon Method)

STORET No: _______

1. Scope and Application

1.1 In this method, NTA refers to the tri-sodium salt of nitrilotriacetic acid, $N(CH_2COONa)_3$.

1.2 This method is applicable to surface waters in the range of 0.5 - 10.0 mg/l NTA.

2. Summary of Method (1)

2.1 Zinc forms a blue-colored complex with 2 carboxy-2'-hydroxy-5'-sulfoformazylbenzene (Zincon) in a solution buffered to pH 9.2. When NTA is added, the Zn-Zincon complex is broken which reduces the optical density in proportion to the amount of NTA present.

3. Sample Handling and Preservation

3.1 Samples should be analyzed as soon as possible, as NTA has been shown to be biodegradable(2).

4. Interferences

4.1 Cations, such as calcium, magnesium, zinc, copper, iron, and manganese, complex with NTA and give a negative interference. These ions are removed by batch treating samples with ion-exchange resin. At concentrations higher than expected in typical river waters(3), only zinc, copper, and iron were not completely removed with ion-exchange treatment. Results are summarized in Table 1.

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TABLE 1

Interference of Common Metals

Metal	mg/1 added	1.0 mg/1 NTA	5.0 mg/1 NTA
		Recoveries	
Blank	0.0	1.1	5.5
Zinc	2.0	<0.5	0.6
Boron	5.0	1.1	5.5
Iron	5.0	0.95	4.6
Molybdenum	2.0	1.0	5.5
Manganese	4.0	1.1	5.6
Aluminum	3.0	0.85	5.2
Copper	0.5	<0.5	3.4
Strontium	5.0	1.0	5.4

4.2 This method has not been found applicable to salt waters.

5. Apparatus

5.1 Shaking machine, tray type, for stirring sample-resin mixtures in 125 ml Erlenmeyer flasks

5.2 Photometer, suitable for measurements at 620 nm.

6. Reagents

6.1 Sodium hydroxide, 6N: Dissolve 120 g NaOH in distilled water and dilute to 500 ml.

6.2 Buffer: Dissolve 31 g boric acid and 37 g potassium chloride in 800 ml distilled water. Adjust pH to 9.2 with 6N NaOH. Dilute to 1 liter.

6.3 Hydrochloric acid, 2N: Dilute 83 ml concentrated HCl to 500 ml with distilled water.

6.4 Zinc: Dissolve 0.44 g $ZnSO_4.7H_2O$ in 100 ml 2N HCl and dilute to 1 liter with distilled water.

6.5 Sodium Hydroxide, 1N: Dissolve 4 g NaOH in distilled water and dilute to 100 ml.

6.6 Zinc-Zincon: Dissolve 0.13 g Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazyl benzene) in 2 ml 1N NaOH (6.5). Add 300 ml buffer (6.2). While stirring, add 15 ml Zinc solution (6.4) and dilute to 1 liter with distilled water.

6.7 Ion-Exchange Resin: Dowex 50W-X8, 50-100 mesh, Na^+ form (or equivalent).

6.8 Stock NTA Solution: Dissolve 1.0700 g $N(CH_2COONa)_3 \cdot H_2O$ in distilled water and dilute to 1 liter. 1.0 ml = 1 mg NTA.

6.9 Working NTA Solution A: Dilute 10 ml Stock NTA solution (6.8) to 100 ml with distilled water. 1 ml = 0.1 mg NTA. Prepare fresh daily.

6.10 Working NTA Solution B: Dilute 10 ml Working NTA Solution A to 100 ml with distilled water. 1 ml = 0.01 mg NTA.

7. Procedure

7.1 Filter approximately 50 ml of well-mixed sample through a 0.45μ membrane filter.

7.2 Prepare a series of standards from 0.5 to 10 mg/l NTA, including a blank of distilled water. Treat standards and blank in same manner as filtered samples.

7.3 To a 25 ml sample in a 125 ml Erlenmeyer flask add approximately 2.5 g ion-exchange resin. Agitate sample for at least 15 minutes.

7.4 Filter through coarse filter paper to remove resin. Pipette 15 ml of filtrate into a 50 ml beaker. Add 25 ml zinc-Zincon by pipette.

7.5 Read absorbance against distilled water at 620 nm in a 1 cm or 2 cm cell.

8. Calculation

8.1 Prepare standard curve by plotting absorbance of standards vs. NTA concentrations. Calculate concentrations of NTA, mg/l, directly from this curve.

9. Precision and Accuracy

9.1 In a single laboratory (AQC), using spiked surface water samples at concentrations of 0.5, 2, 6, and 10 mg/1 NTA, standard deviations were ±0.17, ±0.14, ±0.1, and ±0.16, respectively.

9.2 In a single laboratory (AQC), using spiked surface water samples at concentrations of 1.0 and 7.5 mg/1 NTA, recoveries were 120% and 103%, respectively.

REFERENCES

1. Thompson, J. E. and Duthie, J.R.,"The Biodegradability and Treatment of NTA". Jour. WPCF, 40, No. 2, 306 (1968).

2. Shumate, K. S. et al, "NTA Removal by Activated Sludge - Field Study". ibid., 42, No. 4, 631 (1970).

3. Kopp, J. F. and Kroner, R. C., "Trace Metals in Waters of the United States", USDI, FWPCA, DPS, 1014 Broadway, Cincinnati, Ohio 45202.

NTA

(Automated Zinc-Zincon Method)

STORET No: _______

1. Scope and Application

1.1 In this method, NTA refers to the tri-sodium salt of nitrilotriacetic acid, $N-(CH_2COONa)_3$.

1.2 This method is applicable to surface waters in the range of 0.04 to 1.0 mg/l and 0.5 to 10.0 mg/l NTA, depending on which manifold system is used. It does not apply to saline waters; a positive interference of 0.5 to 1.0 mg/l is present in sewage-type samples.

1.3 Approximately 13 samples per hour can be analyzed.

2. Summary of Method(1)

2.1 Zinc forms a blue-colored complex with 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene (Zincon) in a solution buffered to pH 9.2. When NTA is added, the Zn-Zincon complex is broken which reduces the optical density in proportion to the amount of NTA present.

3. Sample Handling and Preservation

3.1 Samples should be analyzed as soon as possible, as NTA has been shown to be biodegradable.(2)

4. Interferences

4.1 Cations, such as calcium, magnesium, zinc, copper, iron, and manganese, complex with NTA and give a negative interference. These ions are removed automatically by passing the sample through an ion-exchange column. At concentrations higher than expected in typical river waters,(3) only iron was not completely removed by this column treatment. Results, summarized in Tables 1 and 2, show that iron gives a negative interference in concentrations above 3.0 mg/l NTA.

TABLE 1

Interference of Common Metals

Metal	mg/l added	1.0 mg/l NTA	5.0 mg/l NTA
		Recoveries	
Blank	0.0	1.0	5.0
Zinc	2.0	0.9	4.9
Iron*	5.0	0.8	3.8
Manganese	4.0	1.0	4.9
Copper	0.5	1.2	4.9

TABLE 2

Effect of Iron on NTA Recovery in River Water

Iron Added mg/l	NTA Recovered, mg/l (0.5 mg/l added)
0.0	0.52
0.5	0.52
1.0	0.52
2.0	0.52
3.0	0.48
4.0	0.45
5.0	0.39

4.2 At concentration levels below 0.05 mg/l NTA, negative peaking may occur during analyses.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I and II

5.1.2 Manifold

5.1.3 Proportioning pump

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*See Table 2

5.1.4 Colorimeter equipped with 15 mm tubular flow cell and 600 or 625 nm filter.

5.1.5 Recorder

6. Reagents

6.1 Sodium Hydroxide, 6N: Dissolve 120 g NaOH in distilled water and dilute to 500 ml.

6.2 Buffer: Dissolve 31 g boric acid and 37 g potassium chloride in 800 ml distilled water. Adjust pH of solution to 9.2 with 6N NaOH. Dilute to one liter.

6.3 Hydrochloride acid, 2N: Dilute 83 ml concentrated HCl to 500 ml with distilled water.

6.4 Zinc: Dissolve 0.44 g $ZnSO_4 \cdot 7H_2O$ in 100 ml 2N HCl. Dilute to one liter with distilled water.

6.5 Sodium Hydroxide, 1N: Dissolve 4 g NaOH in distilled water and dilute to 100 ml.

6.6 Zinc-Zincon Reagent A (0.04-1.0 mg/l NTA): Dissolve 0.065 g Zincon powder (2-carboxy-2'-hydroxy-5'sulfoformazyl benzene) in 2 ml of 1N NaOH (6.5). Add 300 ml buffer (6.2). Place on a magnetic stirrer and add 7.5 ml zinc solution (6.4). Dilute to one liter with distilled water. This solution is stable for 12 hrs.

6.7 Zinc-Zincon Reagent B (0.5-10 mg/l NTA): Dissolve 0.13 g Zincon in 2 ml 1N NaOH (6.5). Stir on magnetic stirrer. Add 300 ml buffer (6.2) and 15 ml zinc solution (6.4). Stir while mixing. Dilute to 1 liter with distilled water. Stable for one week.

6.8 Ion-Exchange Resin, H^+ Form: 20-50 mesh or 30-80 mesh, Dowex 50W-XB or equivalent.

NOTE: Column is prepared by sucking a water slurry of the resin into 12 inches of 3/16-inch OD sleeving. This may be conveniently done by using a pipette and a loose-fitting glass wool plug in the sleeve.

6.9 Stock NTA Solution: Dissolve 1.0700 g of $N(CH_2CooNa)_3 \cdot H_2O$ in 500 ml of distilled water and dilute to one liter. 1 ml = 1.0 mg NTA.

6.10 Working Solution A: Dilute 10 ml of stock NTA solution to 100 ml with distilled water. 1 ml = 0.1 mg NTA. Prepare daily.

6.11 Working Solution B: Dilute 10 ml of Solution A to 100 ml with distilled water. 1 ml = 0.01 mg NTA. Prepare daily.

6.12 Working Solution C: Dilute 10 ml of Solution B to 100 ml with distilled water. 1 ml = 0.001 mg NTA. Prepare daily.

6.13 Prepare a series of standards by diluting suitable volumes of working solutions to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Solution C/100 ml	Conc., mg NTA/1
2	0.02
4	0.04
6	0.06
8	0.08
10	0.10
ml of Solution B/100 ml	
2	0.20
4	0.40
6	0.60
8	0.80
10	1.00
ml of Solution A/100 ml	
2	2.0
4	4.0
6	6.0
8	8.0
10	10.0

7. Procedure

7.1 Set up manifold as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place wash water tubes in sampler in sets of two, leaving every third position vacant. Set sampling time at 1.5 minutes.

7.4 Place NTA standards in sampler in order of increasing or decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed NTA standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (AQC), using surface water samples at concentrations of 0.1, 0.18, 0.27, and 0.44 mg/l, the standard deviations were ±0.01, ±0.004, ±0.004, ±0.005, respectively. At concentrations of 1.3, 4.0, 5.8, and 7.4 mg/l, the standard deviations were ±0.05, ±0.05, ±0.07, and ±0.1, respectively.

9.2 In a single laboratory (AQC), using surface water samples at concentrations of 0.18 and 0.27 mg/l, recoveries were 101% and 106%, respectively. At concentrations of 4.0 and 5.8 mg/l, the recoveries were 98% and 96%, respectively.

References

1. Thompson, J. E. and Duthie, J. R., "The Biodegradability and Treatment of NTA." Jour. WPCF, 40, No. 2, 306 (1968).

2. Shumate, K. S. et al, "NTA Removal by Activated Sludge - Field Study." ibid, 42, No. 4, 631 (1970).

3. Kopp, J. F. and Kroner, R. C., "Trace Metals in Waters of the United States." USDI, FWPCA, DPS, 1014 Broadway, Cinti, Ohio 45202.

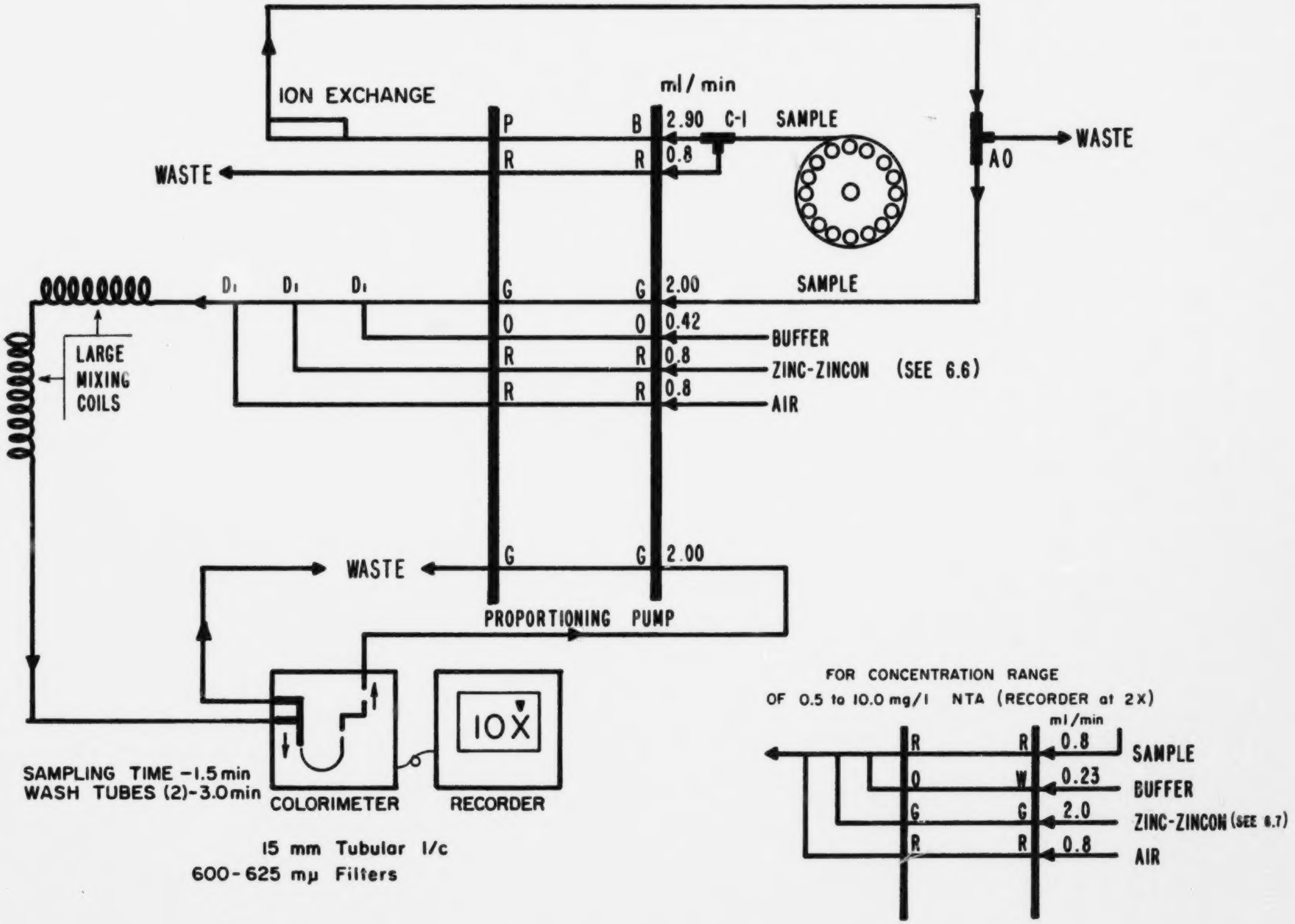
ION EXCHANGE
ml/min
P
R
B 2.90
R 0.8
C-1
SAMPLE
WASTE
A0
WASTE
D₁
D₁
D₁
G
O
R
R
G 2.00
O 0.42
R 0.8
R 0.8
SAMPLE
BUFFER
ZINC-ZINCON (SEE 6.6)
AIR
LARGE MIXING COILS
G
G 2.00
WASTE
PROPORTIONING PUMP
10X
SAMPLING TIME -1.5 min
WASH TUBES (2)-3.0 min
COLORIMETER
RECORDER
15 mm Tubular f/c
600-625 mμ Filters
FOR CONCENTRATION RANGE
OF 0.5 to 10.0 mg/l NTA (RECORDER at 2X)
ml/min
R
O
G
R
R 0.8
W 0.23
G 2.0
R 0.8
SAMPLE
BUFFER
ZINC-ZINCON (SEE 6.7)
AIR

Figure 1. NTA MANIFOLD (0.04-1.0 mg/l NTA)

OIL AND GREASE

1. Scope and Application

STORET NO. 00550

1.1 This method includes the measurement of hexane extractable matter from waters, industrial wastes, and sewages. It is applicable to the determination of relatively non-volatile hydrocarbons, animal fats and waxes, grease and other types of greasy-oily matters.

1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 80°C.

1.3 The method covers the range from 5 to 1000 mg/l of extractable material.

2. Summary of Method

2.1 The sample is acidified to a low pH (<3) and extracted with hexane using a Soxhlet extraction. The solvent is evaporated from the separated extract and the residue weighed.

3. Definitions

3.1 The definition of grease and oil is based on the procedure used. The source of the oil and/or grease, the solvent used, and presence of extractable non-oily matter will influence the material measured and interpretation of results.

4. Purity of Reagents

4.1 Reagent grade hexane shall be used.

5. Sampling and Storage

5.1 A representative sample should be collected in a wide-mouth bottle marked at the 1 liter volume. The initial step of acidification shall be carried out in the sample bottle. The entire sample is used for the test.

5.2 Because losses of grease will occur on sampling equipment, collection of a composite sample is impractical, and the examination of individual

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portions collected at prescribed time intervals must be used to obtain the average concentration over an extended period.

6. Apparatus

6.1 Extraction apparatus consisting of:

6.1.1 Soxhlet Extractor, medium size (Corning No. 3740 or equivalent).

6.1.2 Soxhlet thimbles, to fit in Soxhlet Extractor, 6.1.1.

6.1.3 Flask, 125 ml (Corning No. 4100 or equivalent).

6.1.4 Condenser, Allihn (bulb) type, to fit extractor.

6.2 Vacuum pump, or other source of vacuum.

6.3 Buchner funnel, 12 cm.

7. Reagents

7.1 Sulfuric acid, 1:1. Mix equal volumes of conc. H_2SO_4 and distilled water.

7.2 N-Hexane, b.p. 69°C.

7.3 Filter paper, Whatman No. 40, 11 cm.

7.4 Muslin cloth discs, 11 cm.

7.5 Diatomaceous - silica filter aid suspension, 10 g/l distilled water.

Note 1 - Hyflo Super-Cel (Johns-Manville Corp.) or equivalent is used in the preparation of the filter aid suspension.

8. Procedure

8.1 In the following procedure, all steps must be rigidly adhered to if consistent results are to be obtained.

8.2 Acidify the 1 liter sample with 1:1 H_2SO_4 to a pH below 3. For most samples about 2 ml of the 1:1 acid will be sufficient. Use of a pH sensitive paper is recommended when checking the pH of the sample to avoid possible loss of oil and grease by adherence to glass electrodes.

Note: If the sample has been acidified in the field at the time of collection this step may be omitted.

8.3 Prepare a filter consisting of a muslin cloth disc overlaid with filter paper. Place the assembled filter in the Buchner funnel and wet the filter, pressing down the edges to secure a seal. Using a vacuum, add 100 ml of the filter aid suspension through the filter and then wash with 3-100 ml volumes of distilled water. Continue the vacuum until no more water passes through the filter.

8.4 Filter the acidified sample under vacuum and again continue the vacuum until no more water passes through the filter.

8.5 Remove the filter paper from the funnel with a pair of forceps and carefully place in the Soxhlet thimble. Wipe the sides and bottom of the collecting vessel, the stirring rod, and the Buchner funnel with pieces of filter paper soaked in hexane. Add all pieces of filter paper to the thimble. In general, care must be taken to remove all grease and oil films and to collect all solid material for placement in the thimble.

8.6 Dry the extraction thimble containing the filter paper in an oven at 103°C for exactly 30 minutes. Fill the thimble with small glass beads or glass wool.

8.7 Weigh the extraction flask (pre-dried in oven at 105°C and stored in desiccator), add the hexane, and connect to the Soxhlet apparatus in which the extraction thimble has been placed. Extract at the rate of 20 cycles per hour for four hours. The four hours is timed from the first cycle.

8.8 Distill the solvent from the extraction flask in a water bath at 85°C. Dry by placing the flask on a steam bath and draw air through the flask by means of an applied vacuum for 15 minutes.

8.9 Cool in a desiccator for 30 minutes and weigh.

9. Calculation

9.1 $$\text{mg/l total grease} = \frac{\text{mg increase in weight of flask} \times 1{,}000}{\text{ml sample}}$$

10. Precision and Accuracy

10.1 Precision and accuracy data are not available.

ORGANIC CARBON
(Total and Dissolved)

STORET NUMBERS:
TOTAL: 00680
DISSOLVED: 00681

1. Scope and Application

1.1 This method includes the measurement of organic carbon in surface waters, domestic and industrial wastes, and saline waters. Exclusions are noted under Definitions and Interferences.

1.2 The method is applicable to measurement in the range of 1 to 150 mg/liter.

2. Summary of Method

2.1 A micro sample of the wastewater to be analyzed is injected into a catalytic combusion tube which is enclosed by an electric furnace thermostated at 950°C. The water is vaporized and the carbonaceous material is oxidized to carbon dioxide (CO_2) and steam in a carrier stream of pure oxygen or air. The oxygen flow carries the steam and CO_2 out of the furnace where the steam is condensed and the condensate removed. The CO_2, oxygen, and remaining water vapor enter an infrared analyzer sensitized to provide a measure of CO_2. The amount of CO_2 present is directly proportional to the concentration of carbonaceous material in the injected sample.

3. Definitions

3.1 The carbonaceous analyzer measures all of the carbon in a sample after injection into the combustion tube. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to injection dictates the definition of the carbon as it is measured.

Forms of carbon that are measured by the combustion-infrared method are:

A) soluble, nonvolatile organic carbon; for instance, natural sugars.

B) soluble, volatile organic carbon; for instance, mercaptans.

C) insoluble, partially volatile carbon; for instance, oils.

D) insoluble, particulate carbonaceous materials, for instance, cellulose fibers.

E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.

3.2 The final usefulness or the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment therefore defines the types of carbon which are measured.

4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples (Note 1).

Note 1 - A brief study performed in the AQC Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, it is recommended that the sample be acidified (pH $\leqq$ 2) with HCl or H_2SO_4.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe. The needle openings of the syringe limit the maximum size of particles which may be included in the sample. (Cf 6.3)

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 Dow-Beckman Carbonaceous Analyzer, (single channel) or

6.2.2 Dow-Beckman Carbonaceous Analyzer Model No. 915 (dual channel).

6.3 Hypodermic syringe, 0-50 µl, needle opening of approximately 150 microns; Hamilton No. 705 N or equivalent is satisfactory.

6.3.1 Hamilton No. 750 N, 0-500 µl has a needle opening of approximately 400 microns and may be used for samples containing large particulates.

6.3.2 Hamilton No. CR-700-20 for 20 µl size and No. CR-700-200 for 200 µl size, needle point style No. 3, are push button syringes which insure uniformity of injection rate.

7. Reagents and Materials

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the size of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibility of contamination with organic materials from the resins.

7.2 Potassium Hydrogen Phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in double distilled water and dilute to 100.0 ml.

Note: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium Hydrogen Phthalate, standard solutions: Prepare standard solutions from the stock solution with double distilled water as follows:

ml of Stock Solution Diluted to 100 ml	Standard mg C/liter
1.0	10
2.0	20
3.0	30
4.0	40
5.0	50
6.0	60
8.0	80
10.0	100

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with double distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to 7.3.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

7.7 Packing for total carbon tube. Dissolve 20 g of $Co(NO_3)_2.6H_2O$ (cobalt nitrate hexahydrate) in 50 ml of distilled water. Add this solution to 15 grams of long-fiber asbestos in a porcelain evaporating dish. Mix and evaporate to dryness on a steam bath. Place the dish in a cold muffle furnace and bring to a temperature of 950°C. After one to two hours at this temperature, remove the dish and allow to cool. Break up any large lumps and mix adequately but not excessively. With the combustion tube held in a vertical position, taper joint up, put about 1/2" of untreated asbestos in the tube first, then transfer, in small amounts, approximately one gram of catalyst into the tube with forceps or tweezers. As it is added, tap or push the material gently with a 1/4" glass rod. Do not force the packing. The weight of the rod itself is sufficient to compress the material. When completed, the length of the packing should be about five or six centimeters. Test the packed tube by measuring the flow rate of gas through it at room temperature, and then at 950°C. The rate should not drop more than 20%.

7.8 Packing for carbonate tube, (dual channel instrument). Place a small wad of quartz wool or asbestos near the exit end of the carbonate evolution tube. From the entrance end add 6-12 mesh quartz chips, allowing these to collect against the wad to a length of 10 cm. Pour an excess of 85 percent phosphoric acid into the tube while holding it vertically, and allow the excess to drain out.

8. Instrument Adjustment

8.1 Turn on the infrared analyzer, recorder, and tube furnances, setting the total carbon furnace at 950°C and the carbonate furnace at 175°C. Allow a warm-up time of at least 2 hr. for attainment of stable operation; in daily use the analyzer can be left on continuously. Adjust the oxygen flow rate to 80 to 100 ml/min through the total carbon tube. With the recorder set at the appropriate mv range, adjust the amplifier gain so that a 20-μl sample of the 100 mg/liter carbon standard gives a peak height of approximately half the recorder scale (see 7.3). At this setting the noise level should be less than 0.5 percent of full scale. If the noise level is higher, the analyzer or the recorder may require servicing.

8.1.1 Single channel unit may be equipped with a large-diameter combustion tube and the dual channel unit with a Hastalloy tube for the total carbon channel. In such cases, a 100-μl sample may be injected and appropriate standards in the range of 1 to 30 mg/l carbon used.

9. Calibration - Dual Channel Instrument

9.1 Successively introduce 20 μl of each phthalate standard into the total carbon tube and read the height of the corresponding peak. Between injections allow the recorder pen to return to its base line. The actual injection technique is as follows: Rinse the syringe several times with the solution to be analyzed, fill, and adjust to 20 μl. Wipe off the excess with soft paper tissue, taking care that no lint adheres to the needle. Remove the plug from the syringe holder, insert the sample syringe, and inject the sample into the combusion tube with a single, rapid movement of the index finger. Leave the syringe in the holder until the flow rate returns to normal, then replace it with the plug. Run duplicate determinations on each solution and on a water blank.

9.2 Correct standards for blank correction as follows: Standard peak height minus blank peak height = correct peak height in mm. Prepare a standard curve of total carbon versus peak height.

9.3 In the same way, prepare a series of diluted carbonate standards containing 20, 40, 60, 80, and 100 mg of inorganic carbon per liter. Turn the four-way valve of the apparatus to direct the gas flow through the low temperature tube and to the analyzer. Adjust the flow rate to 80 to 100 ml/min and allow the baseline to become stabilized. Successively introduce 20 µl of each standard and a water blank in duplicate into the low temperature tube and read the peak heights as previously described.

9.4 Prepare a standard curve of inorganic carbon versus peak height applying the correction as noted in 9.2.

10. Procedure - Dual Channel Instrument - Unpreserved samples.

10.1 Mix or blend each sample thoroughly and carry out any appropriate dilution to bring the carbon content within the range of the standard curve.

10.2 Following the technique described in 9.1 and 9.3, inject 20-µl samples successively (in duplicate) into each tube and read the peak heights corresponding to total carbon and inorganic (carbonate) carbon.

From the appropriate calibration curve and each peak height observed, read the corresponding carbon concentration in mg/liter.

10.3 Substract the inorganic carbon value from the total carbon value. The difference thus obtained is operationally defined as Total Organic Carbon. These values may be different from values obtained on acid-blown samples. Results may be verified by operating the unit as a single channel system, i.e., injecting an acidified nitrogen-purged sample into the high temperature furnace side and comparing results.

10.4 Filter a 100 ml aliquot through a pre-rinsed 0.45 μ pore size filter. Repeat sample injection as in 10.2.

10.5 Subtract the dissolved inorganic carbon value from the dissolved carbon value. The difference thus obtained is operationally defined as Dissolved Organic Carbon. These values may be different from values obtained on acid-blown samples. Results may be verified by operating the unit as a single channel system, i.e., injecting an acidified nitrogen-purged sample into the high temperature furnace side and comparing results.

11. Calibration - Single Channel Instrument

11.1 Standardize the instrument according to directions given in 9.1 and 9.2.

12. Procedure - Single Channel Instrument

12.1 Transfer a representative aliquot of about 10 - 15 ml to a 30 ml beaker. If not already acid preserved, add 2 or more drops of concentrated HCl until the pH is reduced to $\leq$ 2 and purge with CO_2-free nitrogen gas for about 5 - 10 minutes (do not use plastic tubing).

Place the beaker on a magnetic stirrer and while stirring withdraw a 20 µl sample. Inject the sample as in 9.1.

12.2 Obtain concentration directly from standard curve. The carbon thus measured is operationally defined as Total Organic Carbon.

12.3 Filter a 100 ml aliquot through a pre-rinsed 0.45 µ pore size filter and proceed as in 12.1.

12.4 Obtain concentration directly from standard curve. The carbon thus measured is operationally defined as Dissolved Organic Carbon.

13. Precision and Accuracy

13.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as	
		Bias, %	Bias, mg/liter
4.9	3.93	+15.27	+ .75
107	8.32	+ 1.01	+1.08

(FWQA Method Study 3, Demand Analyses)

pH

STORET Number: 00400

1. Scope and Application

1.1 This method is applicable to drinking waters and surface waters, domestic and industrial wastes, and saline waters.

2. Summary of Method

2.1 The pH of a sample is an electrometric measurement, using either a glass electrode in combination with a reference potential (saturated calomel electrode) or a combination electrode (glass and reference).

3. Comments

3.1 The sample must be analyzed as soon as practical; preferably within a few hours. Do not open sample bottle before analyses.

3.2 Oil and greases, by coating the pH electrode, may interfere by causing sluggish response.

3.3 At least three buffer solutions must be used to initially standardize the instrument. They should cover the range of pH of the samples to be measured.

3.4 Field pH measurements using comparable instruments are reliable.

4. Precision and Accuracy

4.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

Increment as pH Units	Precision as Standard Deviation pH Units	Accuracy as	
		Bias, %	Bias, pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	--
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

4.2 In a single laboratory (AQC), using surface water samples at an average pH of 7.7, the standard deviation was ± 0.1.

5. Reference

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 276, Method 144A (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p. 280, Method D1293-65 (1970).

PHENOLICS

(4-AAP Method With Distillation)

STORET NO. 32730

1. Scope and Application

   1.1 This method is applicable to the analysis of drinking waters, surface waters, domestic and industrial wastes and saline waters.

   1.2 The method is capable of measuring phenolic materials from about 5 µg/l to about 1000 µg/l when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard.

   1.3 The method is capable of measuring phenolic materials from about 50 µg/l to about 5000 µg/l in the aqueous phase (without solvent extraction) using phenol as a standard.

   1.4 It is not possible to use this method to differentiate between different kinds of phenols.

2. Summary of Method

   2.1 Phenolic materials react with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown colored antipyrine dye. The amount of color produced is a function of the concentration of phenolic material.

3. Comments

   3.1 For most samples a preliminary distillation is required to remove interfering materials.

   3.2 Color response of phenolic materials with 4-aminoantipyrine is not the same for all compounds. Because phenolic type wastes usually contain a variety of phenols, it is not possible to duplicate a mixture of phenols to be used as a standard. For this reason phenol itself has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as phenol. This value will represent the minimum concentration of phenolic compounds present in the sample.

3.3 Control of the pH of the reaction may be accomplished using the procedure detailed in Standard Methods (Page 506, 13th Edition) or ASTM, Part 23, Page 523 (Nov. 1970) or by the use of the ammonium hydroxide-ammonium chloride buffer used in the water hardness test Standard Methods, 13th Edition, Page 181, (1971).

4. Precision and Accuracy

4.1 Using the extraction procedure for concentration of color, six laboratories analyzed samples at concentrations of 9.6, 48.3 and 93.5 μg/l. Standard deviations were, respectively, 0.99, 3.1 and 4.2 μg/l.

4.2 Using the direct photometric procedure, six laboratories analyzed samples at concentrations of 4.7, 48.2 and 97.0 mg/l.

4.3 American Society for Testing and Materials, Part 23, pp. 524-525 Method D-1783-70 (1970).

5. References

The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, pp. 501-510, Method No. 222 through 222E (1971).

American Society for Testing and Materials, Part 23, pp. 519-525, Method D-1783-70 (1970).

PHOSPHORUS, ALL FORMS

(Single Reagent Method)

STORET NO:
SEE TABLE 1

1. Scope and Application

1.1 These methods cover the determination of specified forms of phosphorus in surface waters, domestic and industrial wastes, and saline waters. They may be applicable to sediment-type samples, sludges, algal blooms, etc., but sufficient data is not available at this time to warrant such usage when measurements for phosphorus content are required.

1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are, in turn, defined in Table 1.

1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus, as noted, are determined by calculation.

1.3 The methods are usable in the 0.01 to 0.5 mg/1 P range.

2. Summary of Method

2.1 Ammonium molybdate and potassium antimonyl tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phosphomolybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric-acid-hydrolysis. Organic phosphorus compounds may be

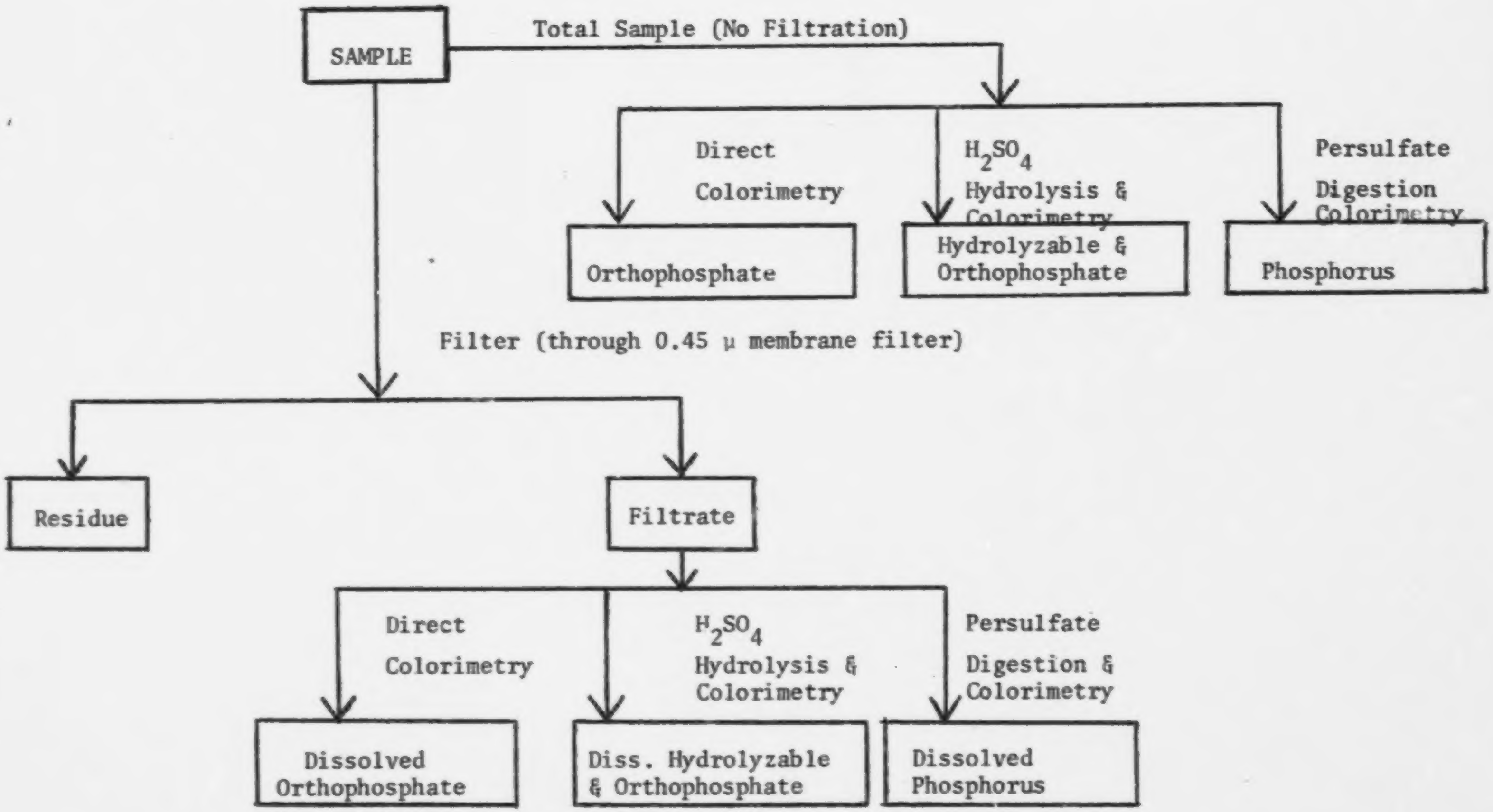
SAMPLE
Total Sample (No Filtration)
Direct Colorimetry
Orthophosphate
H_2SO_4 Hydrolysis & Colorimetry
Hydrolyzable & Orthophosphate
Persulfate Digestion Colorimetry
Phosphorus
Filter (through 0.45 μ membrane filter)
Residue
Filtrate
Direct Colorimetry
Dissolved Orthophosphate
H_2SO_4 Hydrolysis & Colorimetry
Diss. Hydrolyzable & Orthophosphate
Persulfate Digestion & Colorimetry
Dissolved Phosphorus

Figure 1. Analytical Scheme for Differentiation of Phosphorus Forms.

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converted to the orthophosphate form by sulfuric-acid-hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion.(2)

3. Definitions

3.1 The various forms of phosphorus are defined in Table 1.

4. Sampling Handling and Preservation

4.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

4.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.

4.3 If the analysis cannot be performed the same day of collection, the sample should be preserved by the addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C. Note $HgCl_2$ interference under 5.4.

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TABLE 1
PHOSPHORUS TERMINOLOGY

1. Phosphorus (P) - all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure. (00665)
   a. Orthophosphate (P, ortho) - inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure. (00668)
   b. Hydrolyzable Phosphorus (P, hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus predetermined orthophosphates. This hydrolyzable phosphorus includes polyphosphates $[(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] + some organic phosphorus. (00669)
   c. Organic Phosphorus (P, org) - phosphorus (inorganic + oxidizable organic) in the sample as measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)
2. Dissolved Phosphorus (P-D) - all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)
   a. Dissolved Orthophosphate (P-D, ortho) - as measured by the direct colorimetric analysis procedure. (00671)
   b. Dissolved Hydrolyzable Phosphorus (P-D, hydro) - as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates. (00672)
   c. Dissolved Organic Phosphorus (P- D, org) - as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)
3. The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

TABLE 1 (Continued)

a. Insoluble Phosphorus (P-I) = (P) - (P-D). (00667)

(1) Insoluble orthophosphate (P-1, ortho) = (P, ortho) - (P-D, ortho). (00674)

(2) Insoluble Hydrolyzable Phosphorus (P-I, hydro) = (P, hydro) - (P-D, hydro). (00675)

(3) Insoluble Organic Phosphorus (P-I, org) = (P, org) - (P-D, org).(00676)

4. All phosphorus forms shall be reported as P, mg/1, to the third place.

5. Interferences

5.1 It is reported (1) that no interference is caused by copper, iron, or silicate at concentrations many times greater than their greatest reported concentration in sea water. However, high iron concentrations can cause precipitation of phosphorus through the formation of clumps in the bottom of the sample.

5.2 The salt error for samples ranging from 5 to 20 percent salt content was found to be less than 1 percent(1).

5.3 Arsenate, in concentrations greater than found in sea water, does not interfere(1).

5.4 Mercury chloride, used as a preservative, interfers when the chloride level of the sample is low (<50 mg Cl/1). This interference is overcome by spiking samples with a minimum of 50 mg/1 of sodium chloride.

6. Apparatus

6.1 Photometer - A spectrophotometer or filter photometer suitable for measurements at 880 nm, and providing a light path of 1 inch (2.54 cm) or longer, should be used.

6.2 Acid-washed glassware: All glassware used in the determination should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

7. Reagents

7.1 Sulfuric acid solution, 5N: Dilute 70 ml of conc. H_2SO_4 with distilled water to 500 ml.

7.2 Potassium antimonyl tartrate solution: Weigh 1.3715 g $K(SbO)C_4H_4O_6 \cdot 1/2\ H_2O$, dissolve in 400 ml distilled water in 500 ml volumetric flask, dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 20 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 ml distilled water. Store in a plastic bottle at 4°C.

7.4 Ascorbic acid, 0.1M: Dissolve 1.76 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4°C.

7.5 Combined reagent: Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H_2SO_4, 5 ml of potassium antimonyl tartrate solution, 15 ml of ammonium molybdate solution, and 30 ml of ascorbic acid solution. Mix after addition of each reagent.

All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let it stand for a few minutes until the turbidity disappears before processing. The reagent is stable for one week if stored at 4°C.

7.6 Strong-acid solution: Slowly add 310 ml conc. H_2SO_4 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Stock Solution: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate, KH_2PO_4, which has been dried in an oven at 105°C. Dilute the solution to 1.0 l; 1.00 ml equals 0.05 mg P.

7.9 Standard Solution: Dilute 10.0 ml of stock phosphorus solution to 1.0 l with distilled water; 1.00 ml equals 0.5 µg P.

7.9.1 Using standard solution, prepare the following standards in 50.0 ml volumetric flasks:

ml of Standard Solution	Conc., mg/l
0	0.00
1.0	0.01
3.0	0.03
5.0	0.05
10.0	0.10
20.0	0.20
30.0	0.30
40.0	0.40
50.0	0.50

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of strong-acid solution to a 50 ml sample in a 125-ml Erlenmeyer flask.

8.1.2 Add 0.4 gram of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.1.4 Add phenolphathalein and adjust sample to pink with IN NaOH. Bring back to colorless with one drop of strong acid solution. Cool and dilute the sample to 50.0 ml. If sample is not clear at this point, filter.

8.1.5 Determine phosphorus as outlined in 8.3.2 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of strong-acid solution to a 50-ml sample in a 125-ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.2.3 Add phenolphthalein and adjust sample to pink with 1 N NaOH. Bring back to colorless with one drop strong-acid solutions. Cool and dilute the sample to 50 ml.

8.2.4 The sample is now ready for determination of phosphorus as outlined in 8.3.2 Orthophosphate.

8.3 Orthophosphate

8.3.1 Add 1 drop of phenolphthalein indicator to the 50.0 ml sample. If a red color develops, add strong-acid solution drop-wise to just discharge the color.

8.3.2 Add 8.0 ml of combined reagent to sample and mix thoroughly. After a minimum of ten minutes, but no longer than thirty minutes, measure the color absorbance of each sample at 880 nm with a spectrophotometer, using the reagent blank as the reference solution.

9. Calculation

9.1 Prepare standard curve by plotting absorbance values of standards as ordinates and the corresponding phosphorus concentrations as abscissas.

9.1.1 Process standards and blank exactly as the samples. Run at least a blank and two standards with each series of samples. If the standards do not agree within ±2% of the true value, prepare a new calibration curve.

9.2 Obtain concentration value of sample directly from prepared standard curve. Report results as P, mg/l.

10. Precision and Accuracy

10.1 Thirty-three analysts in nineteen laboratories analyzed natural water samples containing exact increments of organic phosphate, with the following results:

Increment as Total Phosphorus mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as	
		Bias, %	Bias, mg P/liter
0.110	0.033	+ 3.09	+.003
0.132	0.051	+11.99	+.016
0.772	0.130	+ 2.96	+.023
0.882	0.128	- 0.92	-.008

(FWPCA Method Study 2, Nutrient Analyses).

10.2 Twenty-six analysts in sixteen laboratories analyzed natural water samples containing exact increments of orthophosphate, with the following results:

Increment as Orthophosphate mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as	
		Bias, %	Bias, mg P/liter
0.029	0.010	-4.95	-.001
0.038	0.008	-6.00	-.002
0.335	0.018	-2.75	-.009
0.383	0.023	-1.76	-.007

(FWPCA Method Study 2, Nutrient Analyses)

References

1. J. Murphy and J. Riley, "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters." Anal. Chim. Acta., 27, 31 (1962).
2. M. Gales, Jr., E. Julian, and R. Kroner, "Method for Quantitative Determination of Total Phosphorus in Water." Jour AWWA, 58, No. 10, 1363 (1966).

PHOSPHORUS, ALL FORMS

(Automated Single Reagent Method)

STORET NO:
SEE TABLE 1

1. Scope and Application

1.1 These methods cover the determination of specified forms of phosphorus in surface waters, domestic and industrial wastes, and saline waters. They may be applicable to sediment-type samples, sludges, algal blooms, etc., but sufficient data is not available at this time to warrant such usage when measurements for phosphorus content are required.

1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are, in turn, defined in Table 1.

1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus, as noted, are determined by calculation.

1.3 The methods are usable in the 0.01 to 1.0 mg P/l range. Approximately 20 samples per hour can be analyzed.

2. Summary of Method

2.1 Ammonium molybdate and potassium antimonyl tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phosphomolybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

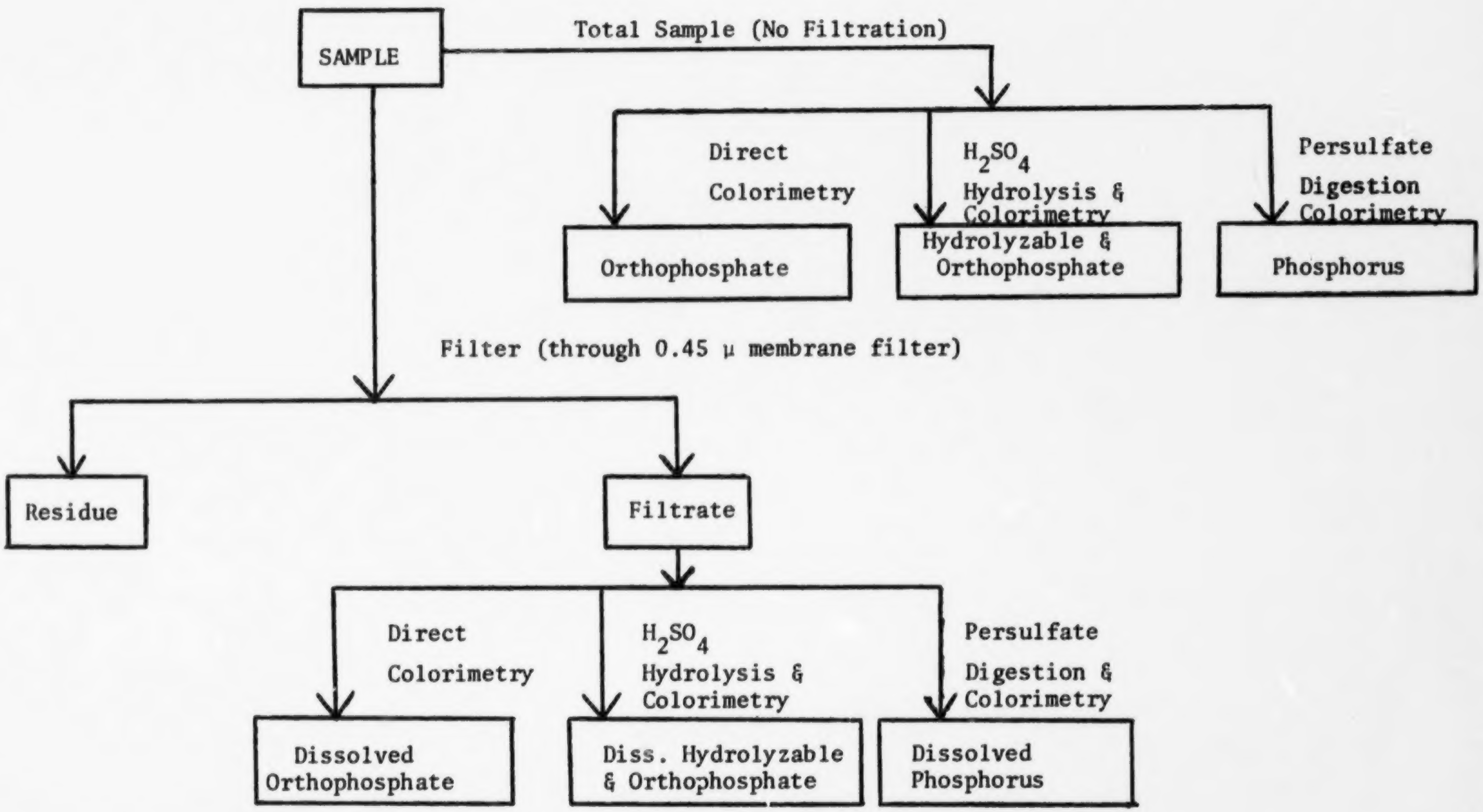
SAMPLE
Total Sample (No Filtration)
Direct
Colorimetry
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Hydrolyzable &
Orthophosphate
Persulfate
Digestion
Colorimetry
Phosphorus
Filter (through 0.45 µ membrane filter)
Residue
Filtrate
Direct
Colorimetry
Dissolved
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Diss. Hydrolyzable
& Orthophosphate
Persulfate
Digestion &
Colorimetry
Dissolved
Phosphorus

Figure 1. Analytical Scheme for Differentiation of Phosphorus Forms.

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2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by manual sulfuric-acid-hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by manual persulfate digestion(2). The developed color is measured automatically on the AutoAnalyzer.

3. Definitions

3.1 The various forms of phosphorus are defined in Table 1.

4. Sample Handling and Preservation

4.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

4.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.

4.3 If the analysis cannot be performed the same day of collection, the sample should be preserved by the addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C. Note $HgCl_2$ interference under 5.4.

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TABLE I: PHOSPHORUS TERMINOLOGY

1. Phosphorus - all of the phosphorus present in the sample regardless of form, as measured by the persulfate digestion procedure. (00665)
    a. Orthophosphate (P-ortho)-inorganic phosphorus $[PO_4]^{-3}$] in the sample as measured by the direct colorimetric analysis procedure. (00668)
    b. Hydrolyzable Phosphorus (P-hydro)-phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphates $[(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] + some organic phosphorus. (00669)
    c. Organic Phosphorus (P-org)-phosphorus (inorganic + oxidizible organic) in the sample as measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)
2. Dissolved Phosphorus (P-D) - all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)
    a. Dissolved Orthophosphate (P-D, ortho) - as measured by the direct colorimetric analysis procedure. (00671)
    b. Dissolve Hydrolyzable Phosphorus (P-D, hydro) - as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates. (00672)
    c. Dissolved Organic Phosphorus (P-D, org) - as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)
3. The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

a. Insoluble Phosphorus (P-I) = (P) - (P-D). (00667)

   (1) Insoluble orthophosphate (P-I, ortho) = (P, ortho) - (P-D, ortho). (00674)

   (2) Insoluble Hydrolyzable Phosphorus (P-I, hydro) = (P, hydro) - (P-D, hydro). (00675)

   (3) Insoluble Organic Phosphorus (P-1, org) = (P, org) - (P-D, org). (00676)

4. All phosphorus forms shall be reported as P, mg/1, to the third place.

5. Interferences

5.1 It is reported(1) that no interference is caused by copper, iron, or silicate at concentrations many times greater than their greatest reported concentration in sea water. However, high iron concentrations can cause precipitation of phosphorus through the formation of clumps in the bottom of the sample.

5.2 The salt error for samples ranging from 5 to 20 percent salt content was found to be less than 1 percent(1).

5.3 Arsenate, in concentrations greater than found in sea water, does not interfere(1).

5.4 Mercury chloride, used as a preservative, interferes. This interference is overcome by substituting a solution of sodium chloride (2.5 g/l) in place of the distilled water (Line YY, 1.20 ml/min).

6. Apparatus

6.1 Technicon AutoAnalyzer consisting of:

6.1.1 Sampler I

6.1.2 Manifold

6.1.3 Proportioning Pump

6.1.4 Heating Bath, 50°C

6.1.5 Colorimeter equipped with 50 mm tubular flow cell and 650 nm filters

6.1.6 Recorder

6.2 Hot Plate or Autoclave

6.3 Acid-washed glassware: All glassware used in the determination should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

7. Reagents

7.1 Sulfuric acid solution, 5N: Dilute 70 ml of conc. H_2SO_4 with distilled water to 500 ml.

7.2 Potassium antimonyl tartrate solution: Weigh 0.3 g $K(SbO)C_4H_4O_6 \cdot 1/2\ H_2O$, dissolve in 50 ml distilled water in 100 ml volumetric flask, dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 4 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 100 ml distilled water. Store in a plastic bottle at 4°C.

7.4 Ascorbic acid, 0.1M: Dissolve 1.8 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4°C.

7.5 Combined reagent: Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H_2SO_4, 5 ml of potassium antimonyl tartrate solution, 15 ml of ammonium molybdate solution, and 30 ml of ascorbic acid solution. Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let it stand for a few minutes until the turbidity disappears before processing. This volume is sufficient for 4 hours operation. Since the stability of this solution is limited, it must be freshly prepared for each run.

7.6 Strong-acid solution: Slowly add 310 ml conc. H_2SO_4 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Wash water: Add 40 ml of strong acid solution (7.6) to 1 liter of distilled water and dilute to 2 liters. (Not to be used when only orthophosphate is being determined).

7.9 Stock Solution: Dissolve 0.4393 g of pre-dried KH_2PO_4 in distilled water and dilute to 1 liter. 1 ml = 0.1 mg P.

7.10 Standard Solution A: Dilute 100 ml of stock solution to 1 liter. 1 ml = 0.01 mg P.

7.11 Standard Solution B: Dilute 100 ml of standard solution A to 1 liter. 1 ml = 0.001 mg P.

7.12 Prepare a series of standards by diluting suitable volumes of standard solutions A and B to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Standard Solution B	Conc., mg P/l
0.0	0.00
2.0	0.02
5.0	0.05
10.0	0.10
ml of Standard Solution A	
2.0	0.20
5.0	0.50
8.0	0.80
10.0	1.00

Note: When the samples to be analyzed are saline waters, Substitute Ocean Water (SOW) should be used for preparing the standards, otherwise, distilled water is used. A tabulation of SOW composition follows:

NaCl	- 24.53g/l	$MgCl_2$	- 5.20g/l	Na_2SO_4	- 4.09g/l
$CaCl_2$	- 1.16g/l	KCl	- 0.70g/l	$NaHCO_3$	- 0.20g/l
KBr	- 0.10g/l	H_3BO_3	- 0.03g/l	$SrCl_2$	- 0.03g/l
NaF	- 0.003g/l				

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of strong-acid solution to a 50 ml sample in a 125-ml Erlenmeyer flask.

8.1.2 Add 0.4 grams of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.1.4 Cool and dilute the sample to 50.0 ml. If sample is not clear at this point, filter.

8.1.5 Determine phosphorus as outlined in 8.3 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of strong-acid solution to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.2.3 Cool and dilute the sample to 50.0 ml. If sample is not clear at this point, filter.

8.2.4 The sample is not ready for determination of phosphorus as outlined in 8.3 Orthophosphate.

8.3 Orthophosphate

8.3.1 Set up manifold as shown in Figure 1.

8.3.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

8.3.3 Place wash water tubes (see 7.8) in Sampler, in sets of 2, leaving every third position vacant. Set sample timing at 1.0 minutes.

8.3.4 Place standards in Sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

8.4.5 Switch sample line from distilled water to Sampler and begin analysis.

9. Calculation

9.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentrations of samples by comparing sample peak heights with standard curve. Any sample whose computed value is less than 5% of its immediate predecessor must be rerun.

10. Precision and Accuracy

10.1 Six laboratories analyzed four natural water samples containing exact increments of orthophosphate, with the following results:

Increment as Orthophosphate mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as	
		Bias, %	Bias, mg P/liter
0.04	0.019	+16.7	+.007
0.04	0.014	- 8.3	-.003
0.29	0.087	-15.5	-.05
0.30	0.066	-12.8	-.04

(FWQA Method Study 4, Automated Methods - In preparation).

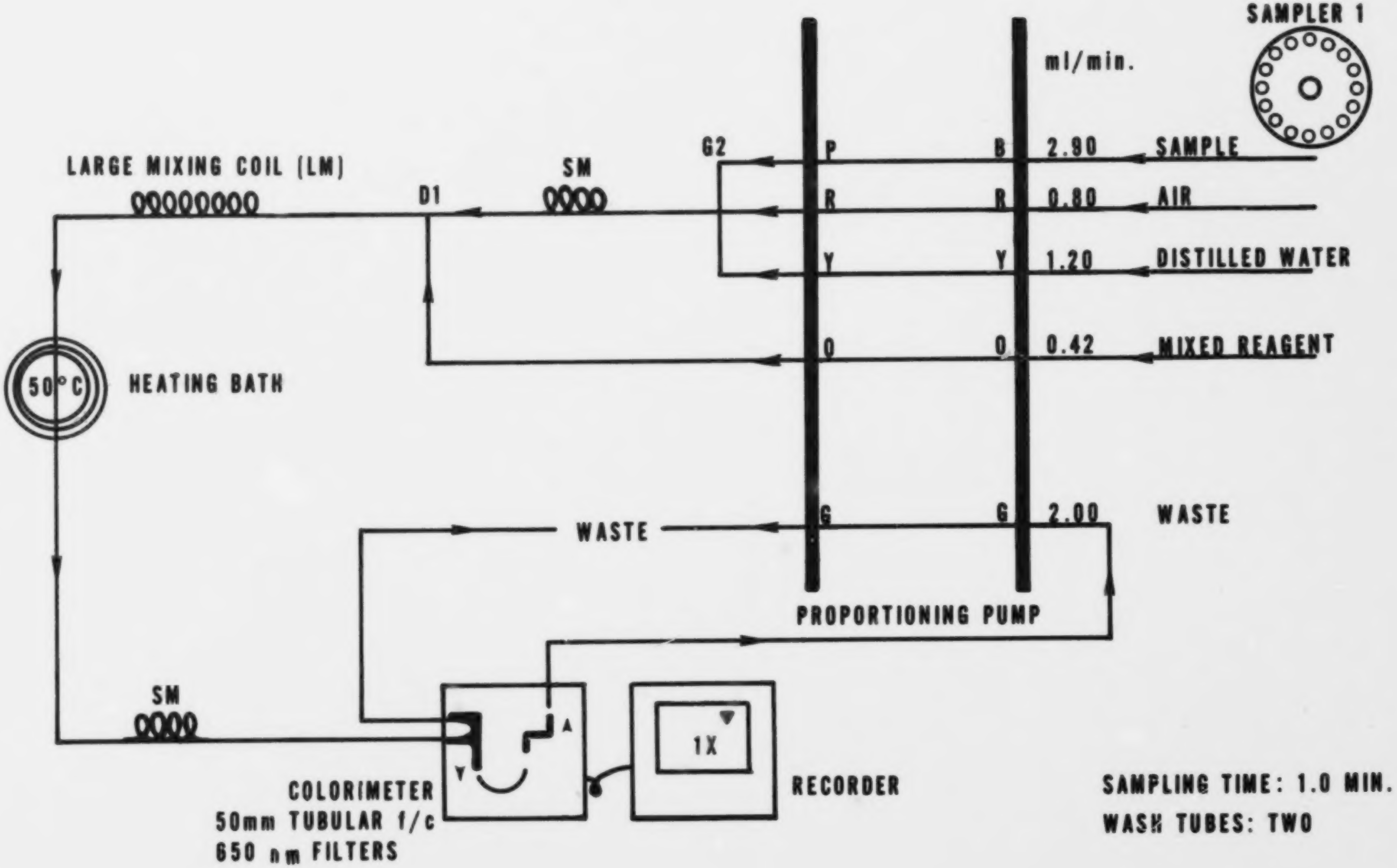
10.2 In a single laboratory, using surface water samples at concentrations of .04, 0.19, 0.35, and 0.84 mg P/1, standard deviations were ±0.005, ±0.000, ±0.003, and ±0.000, respectively (AQC Laboratory).

10.3 In a single laboratory, using surface water samples at concentrations of 0.07 and 0.76 mg P/1, recoveries were 99% and 100%, respectively (AQC Laboratory).

References

1. J. Murphy and J. Riley, "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters." Anal. Chim. Acta., 27, 31 (1962).

2. M. Gales, Jr., E. Julian, and R. Kroner, "Method for Quantitative Determination of Total Phosphorus in Water." Jour AWWA, 58, No. 10, 1363 (1966).


SAMPLER 1
ml/min.
B
2.90
SAMPLE
R
0.80
AIR
Y
1.20
DISTILLED WATER
O
0.42
MIXED REAGENT
G
2.00
WASTE
P
R
Y
O
G
G2
SM
D1
LARGE MIXING COIL (LM)
50°C
HEATING BATH
WASTE
PROPORTIONING PUMP
SM
1X
COLORIMETER
50mm TUBULAR f/c
650 nm FILTERS
RECORDER

SAMPLING TIME: 1.0 MIN.
WASH TUBES: TWO

FIGURE 1. PHOSPHORUS SINGLE REAGENT MANIFOLD

PHOSPHORUS, ALL FORMS

(Automated Stannous Chloride Method)

STORET NO:
SEE TABLE 1

1. Scope and Application

1.1 These methods cover the determination of specified forms of phosphorus in surface waters, domestic and industrial wastes. They may be applicable to sediment-type samples, sludges, algal blooms, etc., but sufficient data is not available at this time to warrant such usage when measurements for phosphorus content are required.

1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are, in turn, defined in Table 1.

1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus, as noted, are determined by calculation.

1.3 The methods are usable in the 0.01 to 1.0 mg P/1 range. Approximately 15 samples per hour can be analyzed.

2. Summary of Method

2.1 Phosphorus is determined by manually digesting the samples with ammonium persulfate and sulfuric acid to convert the various forms of phosphorus to the orthophosphate form and measurement of this orthophosphate on the AutoAnalyzer.

2.2 In this colorimetric method, ammonium molybdate reacts with the orthophosphate in an acid medium to form a heteropoly acid, molybdophosphoric

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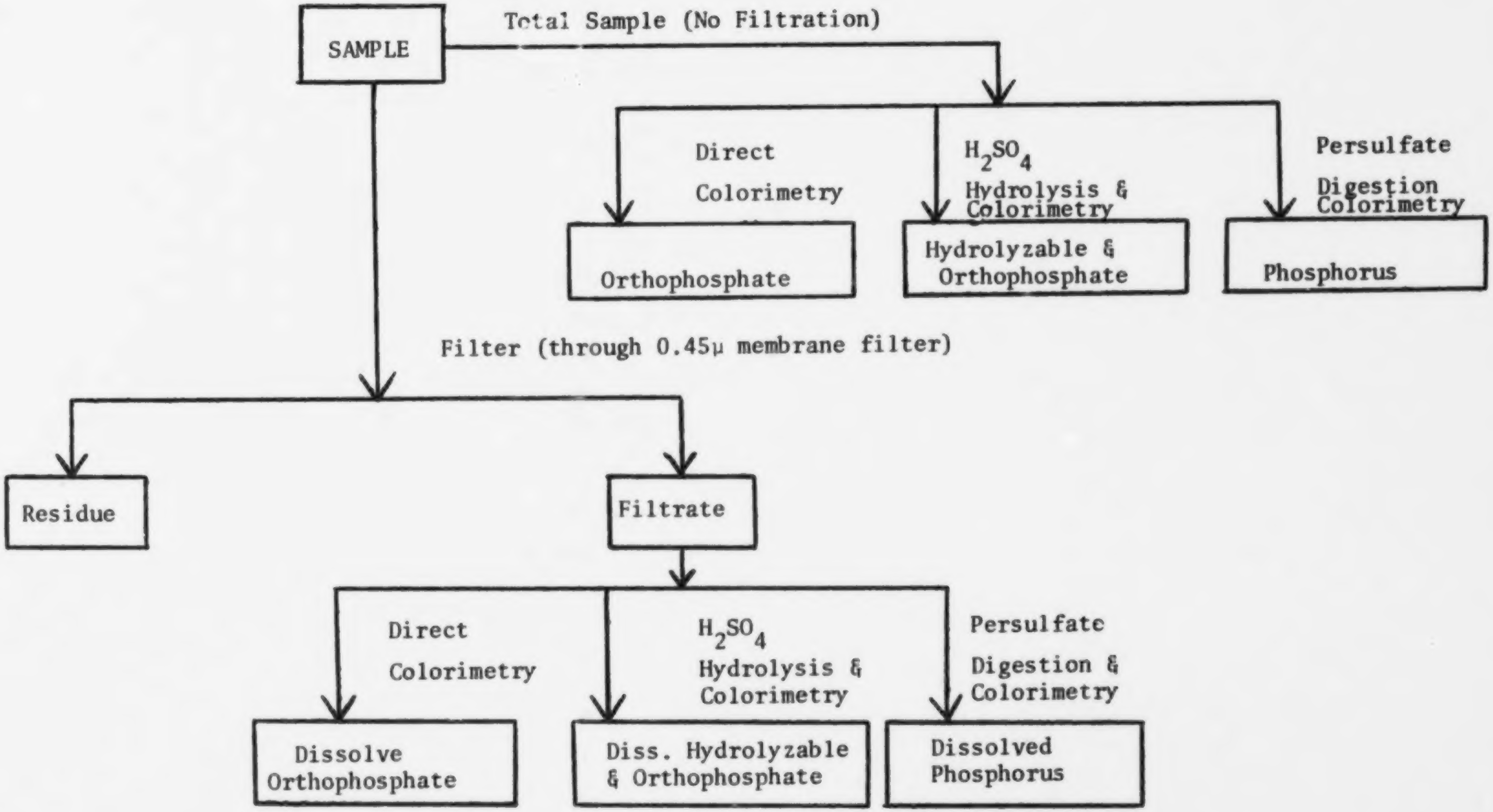
SAMPLE
Total Sample (No Filtration)
Direct
Colorimetry
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Hydrolyzable &
Orthophosphate
Persulfate
Digestion
Colorimetry
Phosphorus
Filter (through 0.45μ membrane filter)
Residue
Filtrate
Direct
Colorimetry
Dissolve
Orthophosphate
H_2SO_4
Hydrolysis &
Colorimetry
Diss. Hydrolyzable
& Orthophosphate
Persulfate
Digestion &
Colorimetry
Dissolved
Phosphorus

Figure 1. Analytical Scheme for Differentiation of Phosphorus Forms

acid. This acid is reduced by stannous chloride to form the intensely colored complex, molybdenum blue, which is directly proportional to the amount of phosphorus.

3. Definitions

3.1 The various forms of phosphorus are defined in Table 1.

4. Sample Handling and Preservation

4.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.

4.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.

4.3 If the analysis cannot be performed the same day of collection, the sample should be preserved by the addition of 40 mg $HgCl_2$ per liter and refrigeration at 4°C.

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TABLE 1
PHOSPHORUS TERMINOLOGY

1. Phosphorus (P) - all of the phosphorus present in the sample regardless of form, as measured by the persulfate digestion procedure. (00665)
    a. Orthophosphate (P, ortho)-inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure. (00668)
    b. Hydrolyzable Phosphorus (P, hydro)-phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphates $[(P_2O_7)^{-4}, (P_3O_{10})^{-5}$, etc.] + some organic phosphorus. (00669).
    c. Organic Phosphorus (P,org)-phosphorus (inorganic + oxidizable organic) in the sample as measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)
2. Dissolved Phosphorus (P-D) - all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)
    a. Dissolved Orthophosphate (P-D, ortho) - as measured by the direct colorimetric analysis procedure. (00671)
    b. Dissolved Hydrolyzable Phosphorus (P-D, hydro) - measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates. (00672)
    c. Dissolved Organic Phosphorus (P-D, org) - as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)
3. The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

a. Insoluble Phosphorus = (P) - (P-D). (00667)

(1) Insoluble orthophosphate (P-I, ortho) = (P, ortho) - (P-D, ortho). (00674)

(2) Insoluble Hydrolyzable Phosphorus (P-I, hydro) = (P, hydro) - (P-D, hydro). (00675)

(3) Insoluble Organic Phosphorus (P-I, org) = (P, org) - (P-D, org). (00676)

4. All phosphorus forms shall be reported as P, mg/l, to the third place.

5. Interferences

5.1 Method does not work on saline waters.

6. Apparatus

6.1 Acid-washed glassware: To prevent contamination, all glassware used in the preparation of standards and actual determinations should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

6.2 Technicon AutoAnalyzer consisting of:

6.2.1 Sampler I.

6.2.2 Continuous Filter.

6.2.3 Manifold

6.2.4 Proportioning Pump.

6.2.5 Colorimeter equipped with 15 mm tubular flow cell and 650 nm filters.

6.2.6 Recorder.

6.3 Hot Plate or Autoclave

7. Reagents

7.1 Sulfuric acid solution: Cautiously add 310 ml of concentrated sulfuric acid slowly and with stirring to about 600 ml of distilled water. Cool and dilute to 1 liter.

7.2 Ammonium molybdate solution: Dissolve 12.5 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 175 ml of distilled water. Cautiously add 77.5 ml of concentrated sulfuric acid slowly and with stirring to 400 ml of distilled water. Cool. Add the molybdate solution to the acid solution and dilute to 1 liter.

7.3 Stannous chloride solution: Dissolve 2.5 g of fresh $SnCl_2.2H_2O$ in 20 ml of hydrochloric acid. Warming on a hot plate will aid in dissolving this material. Dilute to 400 ml. Stable for 1 week at room temperature; one month at 4°C.

7.4 Wash water: Add 40 ml of sulfuric acid solution (Reagent 7.1) to 1 liter of distilled water and dilute to 2 liters.

7.5 Stock Solution: Dissolve 0.4393 g of pre-dried KH_2PO_4 in distilled water and dilute to 1 liter. 1 ml = 0.1 mg P.

7.6 Standard Solution A: Dilute 100 ml of stock solution to 1 liter. 1 ml = 0.01 mg P.

7.7 Standard Solution B: Dilute 100 ml of standard solution A to 1 liter. 1 ml = 0.001 mg P.

7.8 Prepare a series of standards by diluting suitable volumes of standard solutions A and B to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Standard Solution B	Conc., mg P/1
1.0	0.01
2.0	0.02
5.0	0.05
10.0	0.10
ml of Standard Solution A	
2.0	0.20
5.0	0.50
8.0	0.80
10.0	1.00

7.9 Ammonium persulfate, reagent grade.

7.10 NaOH-EDTA Solution: Dissolve 65 g NaOH and 6 g EDTA in distilled water and dilute to 1 liter.

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of sulfuric acid solution to a 50-ml sample in a 125-ml Erlenmeyer flask.

8.1.2 Add 0.4 g ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.1.4 Cool and dilute the sample to 50.0 ml. If sample is not clear at this point, filter.

8.1.5 The sample is now ready for automatic analysis as outlined in 8.3 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of sulfuric acid solution to a 50-ml sample in a 125-ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for approximately 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi).

8.2.3 Cool and dilute the sample to 50.0 ml. If sample is not clear at this point, filter.

8.2.4 The sample is now ready for automatic analysis as outlined in 8.3 Orthophosphate.

8.3 Orthophosphate

8.3.1 Set up manifold as shown in Figure 1.

8.3.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

8.3.3 Place wash water tubes (see 7.4) in alternate openings in Sampler and set sample timing at 2.0 minutes. Use distilled water, instead of acid-wash water when only orthophosphate is being determined.

8.3.4 Place standards in Sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

8.3.5 Switch sample line from distilled water to Sampler and begin analysis.

8.3.6 At end of run, clean out manifold system with NaOH-EDTA solution.

9. Calculations

9.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

10. Precision and Accuracy

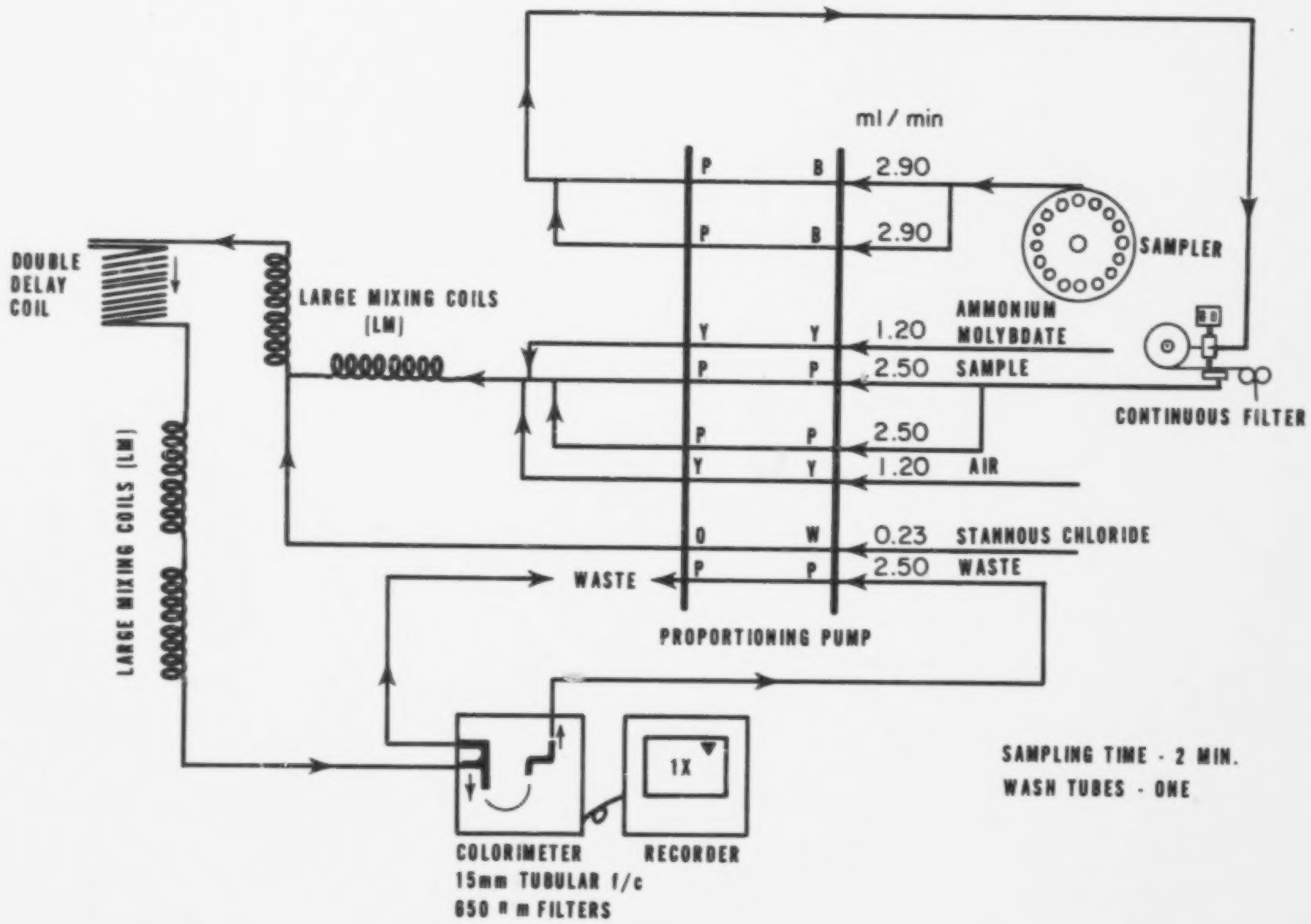
10.1 In a single laboratory, using surface water samples at concentrations of 0.06, 0.11, 0.48, and 0.62 mg P/1, the standard deviation was ±0.004 (AQC Laboratory).

10.2 In a single laboratory, using surface water samples at concentrations of 0.11 and 0.74 mg P/1, recoveries were 90% and 95%, respectively (AQC Laboratory).

References

1. Standard Methods for the Examination of Water and Wastewater, 12th Edition, p. 234, Amer. Pub. Health Assoc., Inc., New York, N.Y. (1965).

2. M. Gales, Jr., E. Julian, and R. Kroner, "Method for Quantitative Determination of Total Phosphorus in Water." Jour. AWWA, 58, No. 10, 1363 (1966).


ml / min
2.90
2.90
1.20
2.50
2.50
1.20
0.23
2.50
P
P
Y
P
P
Y
O
P
B
B
Y
P
P
Y
W
P
SAMPLER
AMMONIUM MOLYBDATE
SAMPLE
CONTINUOUS FILTER
AIR
STANNOUS CHLORIDE
WASTE
WASTE
PROPORTIONING PUMP
DOUBLE DELAY COIL
LARGE MIXING COILS (LM)
LARGE MIXING COILS (LM)
1X
COLORIMETER
15mm TUBULAR f/c
650 n m FILTERS
RECORDER

SAMPLING TIME - 2 MIN.
WASH TUBES - ONE

FIGURE 1 - PHOSPHORUS MANIFOLD

SELENIUM

(Diaminobenzidine Method)

STORET NUMBERS:
DISSOLVED 01145
TOTAL 01147

1. Scope and Application

1.1 This colorimetric method covers the determination of selenium in drinking waters and surface waters, domestic and industrial wastes, and saline waters.

1.2 The method covers the range from 0.003 - 0.05 mg selenium per liter.

2. Summary of Method

2.1 All selenium compounds present in the sample are first oxidized to selenate by acid permanganate. The selenate is then reduced to selenite. Addition of diaminobenzidine reagent forms the piazselenol complex which is subsequently extracted into toluene and the absorbance measured at 420 nm. The piazselenol color is stable, but evaporation of toluene concentrates the color to a marked degree in a few hours.

3. Comments

3.1 For the measurement of dissolved selenium, the sample must first be filtered through a 0.45 μ membrane filter.

3.2 Evaporation of solutions of sodium selenate to complete dryness can result in substantial loss of selenium unless calcium has been added to the sample.

3.3 Temperature, time, and acid concentrations are critical to obtain quantitative reduction without loss of selenium. The optimum pH for the formation of piazselenol is approximately 1.5.

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3.4 No inorganic compounds are known to give a positive interference. Negative interference results from compounds that lower the concentration of diaminobenzidine by oxidizing this reagent. The addition of EDTA eliminates negative interference from at least 2.5 mg ferric iron. Iodine, and to a lesser extent bromide, causes low results.

3.5 When iodide or bromide interferences are encountered, a distillation step is required. This entails the addition of 50 ml $KBr-H_2SO_4$ reagent and 1 ml 30% H_2O_2 to the residue remaining after the evaporation step. The mixture is distilled until the color of bromine is gone from the flask. Diaminobenzidine is then added to the distillate and the piazselenol complex extracted into toluene.

4. Precision and Accuracy

4.1 A synthetic unknown sample containing 20 μg/l Se, 40 μg/l As, 250 μg/l Be, 240 μg/l B, and 6 μg/l V in distilled water was determined by the diaminobenzidine method, with a relative standard deviation of 21.2% and a relative error of 5.0% in 35 laboratories.

5. Reference

5.1 The procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 296 Method 150 A (1971).

SILICA, DISSOLVED

STORET NUMBER: 00955

1. Scope and Application

   1.1 This method is applicable to drinking waters and surface waters, domestic and industrial wastes, and saline waters.

   1.2 Working range of method is approximately 2 to 25 mg silica/l. The upper range can be extended by taking suitable aliquots; the lower range can be extended by the addition of amino-naphthol-sulfonic acid solution, as described in ASTM reference.

2. Summary of Method

   2.1 A well-mixed sample is filtered through a 0.45 µ membrane filter. The filtrate, upon the addition of molybdate ion in acidic solution, forms a greenish-yellow color complex proportional to the dissolved silica in the sample. The color complex is then measured spectrophotometrically.

3. Comments

   3.1 Excessive color and/or turbidity interfere. Correct by running blanks prepared without addition of the ammonium molybdate solution.

4. Precision and Accuracy

   4.1 Photometric evaluations by the amino-naphthol-sulfonic acid procedure have an estimated precision of ±0.10 mg/l in the range from 0 to 2 mg/l (ASTM).

   4.2 Photometric evaluation of the silico-molybdate color in the range from 2 to 50 mg/l have an estimated precision of approximately 4 percent of the quantity of silica measured (ASTM).

5. Reference

5.1 The procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 303, Method 151B (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p. 91, Method D859-68 (1970).

SOLIDS, FILTERABLE (DISSOLVED)

STORET NO. 70300

1. Scope and Application

   1.1 This method is applicable to surface waters, domestic and industrial wastes, and saline waters.

   1.2 The practical range of the determination is 10 mg/l to 20,000 mg/l.

2. Summary of Method

   2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.

3. Definitions

   3.1 Filterable solids are defined as those solids capable of passing through a standard glass fiber filter and dried to constant weight at 180°C.

4. Sample Handling and Preservation

   4.1 Samples should be analyzed as soon as practicable.

5. Interferences

   5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying and desiccation and quick weighing.

   5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.

   5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

6. Apparatus

   6.1 Glass fiber filter discs, 4.7 cm or 2.2 cm, without organic binder, Reeve Angel type 984 H, Gelman type A, or equivalent.

6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.

6.3 Suction flask, 500 ml.

6.4 Gooch crucibles, 25 ml (if 2.2 cm filter is used).

6.5 Evaporating dishes, porcelain, 100 ml volume. (Vycor or platinum dishes may be substituted).

6.6 Steam bath.

6.7 Drying oven, 180°C±2°C.

6.8 Desiccator.

6.9 Analytical balance, 200 g capacity, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103-105°C for one hour. Remove to desiccator and store until needed.

7.2 Preparation of evaporating dishes: Heat the clean dish to 550°C for one hour in a muffle furnace. Cool in desiccator and store until needed. Weigh immediately before use.

7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml volumetric cylinder. If suspended matter is low, a larger volume may be filtered.

7.4 Filter the sample through the glass fiber filter and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

7.5 Transfer 100 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

7.6 Dry the evaporated sample for at least one hour at 180±2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

7.7 Note: The filtrate from the test for SOLIDS, NON-FILTERABLE, may be used for this determination.

8. Calculation

8.1 Calculate filterable solids as follows:

$$\text{Filt. solids, mg/l} = \frac{(\text{Wt. of dried residue + dish}) - (\text{wt. of dish}) \times 1000}{\text{Volume of filtrate used}}$$

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual sample cannot be obtained.

SOLIDS, NON-FILTERABLE (SUSPENDED)

1. Scope and Application

STORET NO. 00530

1.1 This method is applicable to surface waters, domestic and industrial wastes, and saline waters.

1.2 The practical range of the determination is 20 mg/l to 20,000 mg/l.

2. Summary of Method

2.1 A well-mixed sample is filtered through a standard glass fiber filter, and the residue retained on the filter is dried to constant weight at 103-105°C.

3. Definitions

3.1 Non-filterable solids are defined as those solids which are retained by a standard glass fiber filter and dried to constant weight at 103-105°C.

4. Sample Handling and Preservation

4.1 Non-homogenous particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample.

4.2 Preservation of the sample is not practical; analysis should begin as soon as possible.

5. Interferences

5.1 Too much residue on the filter will entrap water and may require prolonged drying.

6. Apparatus

6.1 Glass fiber filter discs, 4.7 cm or 2.2 cm, without organic binder, Reeve Angel type 984 H, Gelman type A, or equivalent.

6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.

6.3 Suction flask, 500 ml.

6.4 Gooch crucibles, 25 ml (if 2.2 cm filter is used).

6.5 Drying oven, 103-105°C.

6.6 Desiccator.

6.7 Analytical balance, 200 g capacity, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103-105°C for one hour. Remove to desiccator and store until needed. Weigh immediately before use.

7.2 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml volumetric cylinder. If suspended matter is low, a larger volume may be filtered.

7.3 Carefully remove the filter from the membrane filter funnel assembly. Alternatively, remove crucible and filter from crucible adapter. Place in drying oven and dry at 103-105°C to constant weight.

8. Calculations

8.1 Calculate non-filterable solids as follows:

$$\text{Non-filterable solids, mg/l} = \frac{(\text{Wt. of filter + residue})-(\text{wt. of filter}) \times 1000}{\text{ml of sample filtered}}$$

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

SOLIDS, TOTAL

STORET NO. 00500

1. Scope and Application

   1.1 This method is applicable to surface waters, domestic and industrial wastes, and saline waters.

   1.2 The practical range of the determination is from 10 mg/l to 30,000 mg/l.

2. Summary of Method

   2.1 A well mixed aliquot of the test sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105°C.

3. Definitions

   3.1 Total Solids are defined as the sum of the homogenous suspended and dissolved materials in a sample.

4. Sample Handling and Preservation

   4.1 Samples should be analyzed as soon as practicable.

5. Interferences

   5.1 Large, floating particles or submerged agglomerates (non-homogenous materials) should be excluded from the test sample.

   5.2 Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.

6. Apparatus

   6.1 Evaporating dishes, porcelain, 90 mm, 100-ml capacity. (Vycor or platinum dishes may be substituted and smaller size dishes may be used if required.)

7. Procedure

   7.1 Heat the clean evaporating dish to 550±50°C for 1 hour in a muffle furnace. Cool, desiccate, weigh and store in desiccator until ready for use.

7.2 Transfer a measured aliquot of sample to the pre-weighed dish and evaporate to dryness on a steam bath or in a drying oven.

7.2.1 Choose an aliquot of sample sufficient to contain a residue of at least 25 mg. To obtain a weighable residue, successive aliquots of sample may be added to the same dish.

7.2.2 If the evaporation is performed in a drying oven, the temperature should be lowered to approximately 98°C to prevent boiling and splattering of the sample.

7.3 Dry the evaporated sample for at least 1 hour at 103-105°C. Cool in a desiccator and weigh. Repeat the cycle of drying at 103-105°C, cooling, desiccating and weighing until a constant weight is obtained or until loss of weight is less than 4% of the previous weight, or 0.5 mg, whichever is less.

8. Calculation

8.1 Calculate total solids as follows:

$$\text{Total Solids, mg/l} = \frac{(\text{Wt. of sample + dish - wt. of dish})\ 1000}{\text{Vol. of Sample}}$$

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

SOLIDS, VOLATILE

STORET No: 00505

1. Scope and Application

1.1 This method determines the weight of solid material combustible at 550°C.

1.2 The test is useful in obtaining a rough approximation of the amount of organic matter present in the solid fraction of sewage, activated sludge, industrial wastes, or bottom sediments.

2. Summary of Method

2.1 The residue obtained from the determination of total, suspended, or dissolved solids is ignited at 550°C in a muffle furnace. The loss of weight on ignition is reported as mg/l volatile solids.

3. Comments

3.1 The test is subject to many errors due to loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

3.2 The results should not be considered an accurate measure of organic carbon in the sample, but maybe useful in the control of plant operations.

3.3 The principal source of error in the determination is failure to obtain a representative sample.

4. Precision and Accuracy

A collaborative study involving three laboratories examining four samples by means of ten replicates showed a standard deviation of ±11 mg/l at 170 mg/l volatile solids concentration. (Reference)

5. Reference

The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, P. 538, Method 224D (1971).

SPECIFIC CONDUCTANCE

STORET NUMBER: 00095

1. Scope and Application

1.1 This method is applicable to drinking waters and surface waters, domestic and industrial wastes, and saline waters.

2. Summary of Method

2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.

2.2 Samples are preferably analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C.

3. Comments

3.1 Instrument must be standardized with KCl solution before daily use.

3.2 Conductivity cell must be kept clean.

3.3 Field measurements with comparable instruments are reliable.

4. Precision and Accuracy

4.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results:

Increment as Specific Conductance µmhos/cm	Precision as Standard Deviation µmhos/cm	Accuracy as	
		Bias, %	Bias, µmhos/cm
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

(FWPCA Method Study 1, Mineral and Physical Analyses).

4.2 In a single laboratory (AQC), using surface water samples with an average conductivity of 536 µmhos/cm @ 25°C, the standard deviation was ±6.

5. References

5.1 The procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 323, Method 154 (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p. 179, Method D1125-64 (1970).

SULFATE

STORET NUMBER: 00945

1. Scope and Application

1.1 This method is applicable to drinking waters and surface waters, domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4/l.

2. Summary of Method

2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a photoelectric colorimeter or spectrophotometer and compared to a curve prepared from standard sulfate solutions.

2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.

3. Comments

3.1 Proprietary reagents, such as Hach SULFAVER or equivalent, are acceptable.

4. Precision and Accuracy

4.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate, with the following results:

Increment as Sulfate mg/liter	Precision as Standard Deviation mg/liter	Accuracy as	
		Bias, %	Bias, mg/liter
8.6	2.30	-3.72	-.3
9.2	1.78	-8.26	-.8
110	7.86	-3.01	-3.3
122	7.50	-3.37	-4.1
188	9.58	+0.04	+.1
199	11.8	-1.70	-3.4

(FWPCA Method Study 1, Mineral and Physical Analyses).

5. Reference

5.1 The procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 334, Method 156C (1971).

ASTM Standards, Part 23, Water; Atmospheric Analysis, p. 54, Method D516-68 (1970).

SULFATE

(Automated Chloranilate Method)

STORET NO. 00945

1. Scope and Application

1.1 This automated method is applicable to surface waters, domestic and industrial wastes, and saline waters, in the range of 10 to 400 mg SO_4/l. Approximately 15 samples per hour can be analyzed.

2. Summary of Method

2.1 When solid barium chloranilate is added to a solution containing sulfate, barium sulfate is precipitated, releasing the highly colored acid chloranilate ion. The color intensity in the resulting chloranilic acid is proportional to the amount of sulfate present.

3. Sample Handling and Preservation

3.1 No special requirements.

4. Interferences

4.1 Cations, such as calcium, aluminum, and iron, interfere by precipitating the chloranilate. These ions are removed automatically by passage through an ion exchange column.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I.

5.1.2 Continuous filter.

5.1.3 Manifold.

5.1.4 Proportioning pump.

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.

5.1.6 Recorder.

5.1.7 Heating bath, 45°C.

5.2 Magnetic stirrer.

6. Reagents

6.1 Barium chloranilate: Add 9 g of barium chloranilate ($BaC_6Cl_2O_4$) to 333 ml of ethyl alcohol and dilute to 1 liter with distilled water.

6.2 Acetate buffer, pH 4.63: Dissolve 13.6 g of sodium acetate in distilled water. Add 6.4 ml of acetic acid and dilute to 1 liter with distilled water. Make fresh weekly.

6.3 NaOH-EDTA Solution: Dissolve 65 g of NaOH and 6 g of EDTA in distilled water and dilute to 1 liter.

Note: This solution is also used to clean out manifold system at end of sampling run.

6.4 Ion Exchange Resin: Dowex-50 W-X8, ionic form $-H^+$.

Note: Column is prepared by sucking a slurry of the resin into 12 inches of 3/16-inch OD sleeving. This may be conveniently done by using a pipette and a loose-fitting glass wool plug in the sleeve. The column, upon exhaustion, turns red.

6.5 Stock solution: Dissolve 1.4790 g of pre-dried Na_2SO_4 in distilled water and dilute to 1 liter. 1 ml = 1 mg.

6.5.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/l
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
15.0	150
20.0	200
30.0	300
40.0	400

7. Procedure

7.1 Set up manifold as shown in Figure 1. (Note that any precipitated $BaSO_4$ and the unused barium chloranilate are removed by filtration. If any $BaSO_4$ should come through the filter, it is complexed by the NaOH-EDTA reagent).

7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (AQC), using surface water samples at concentrations of 39, 111, 188, and 294 mg SO_4/l, the standard deviations were

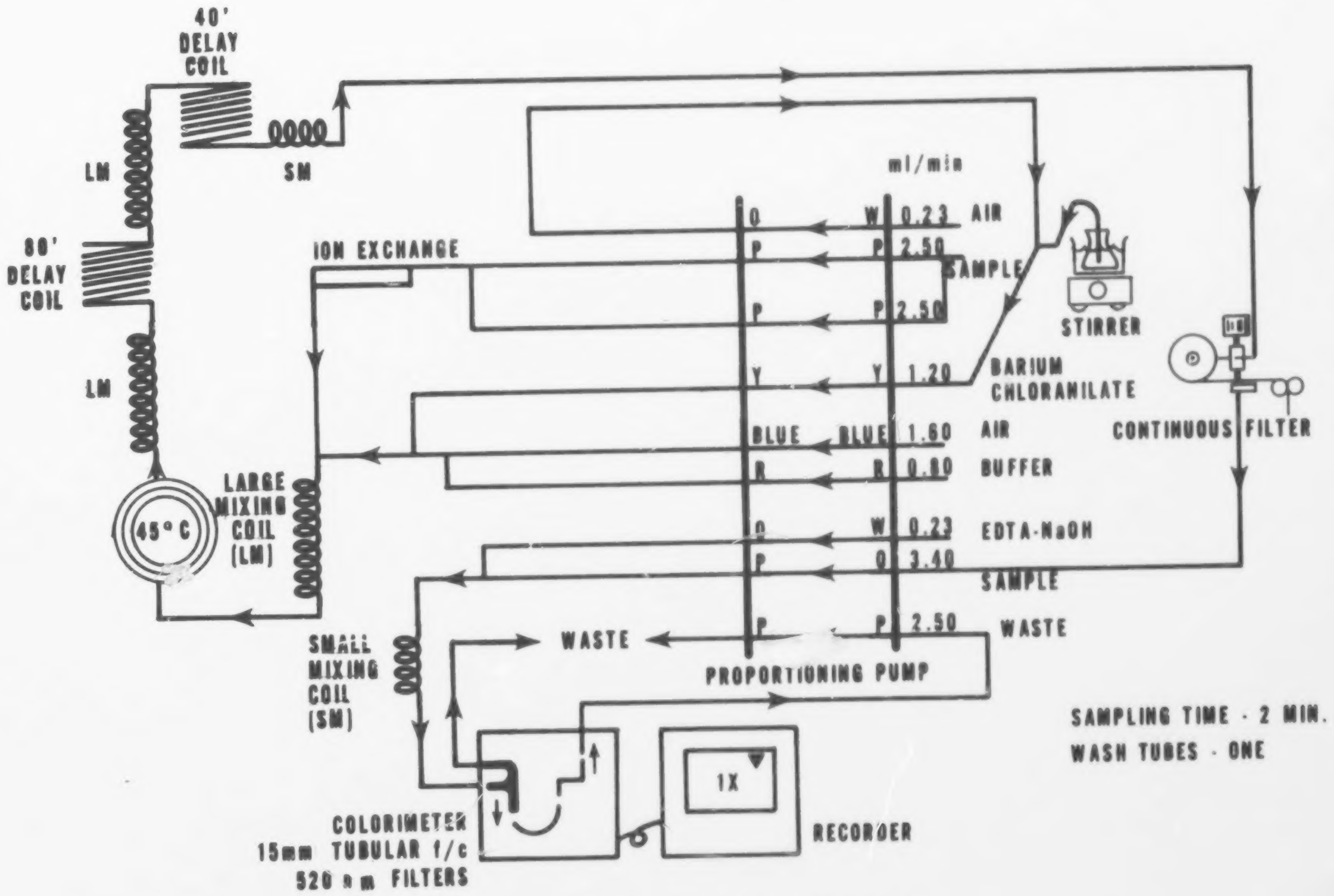
±0.6, ±1.0, ±2.2, and ±0.8, respectively.

9.2 In a single laboratory (AQC) using surface water samples at concentrations of 82 and 295 mg SO_4/1, recoveries were 99% and 102%, respectively.

Reference

1. R.J. Bertolocini and J.E. Barney, Anal. Chem., 29, 283 (1957).

2. M.E. Gales, Jr., W.H. Kaylor and J.E. Longbottom, "Determination of Sulphate by Automatic Colorimetric Analysis." Analyst, 93, 97 (1968).


40' DELAY COIL
SM
LM
80' DELAY COIL
LM
45° C
LARGE MIXING COIL (LM)
ION EXCHANGE
ml/min
O
W 0.23 AIR
P
P 2.50 SAMPLE
P
P 2.50
STIRRER
Y
Y 1.20 BARIUM CHLORANILATE
BLUE
BLUE 1.60 AIR
R
R 0.80 BUFFER
O
W 0.23 EDTA-NaOH
P
O 3.40 SAMPLE
P
P 2.50 WASTE
CONTINUOUS FILTER
WASTE
PROPORTIONING PUMP
SMALL MIXING COIL (SM)
1X
RECORDER
COLORIMETER
15mm TUBULAR f/c
520 nm FILTERS

SAMPLING TIME - 2 MIN.

WASH TUBES - ONE

FIGURE 1 - SULFATE MANIFOLD

SULFIDE

Titrimetric (Iodine) Method

STORET NO. ______
Total: 00745
Dissolved: 00746

1. Scope and Application

   1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking waters, surface waters, domestic and industrial wastes, and saline waters.

   1.2 Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class).

   1.3 This method is suitable for the measurement of sulfide in concentrations above 1 mg/l.

2. Summary of Method

   2.1 Sulfides are stripped from the acidified sample with an inert gas and collected in a zinc acetate solution. Excess iodine added to the zinc sulfide suspension reacts with the sulfide under acidic conditions. Thiosulfate is used to measure unreacted iodine to indicate the quantity of iodine consumed by sulfide.

3. Comments

   3.1 Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances will give high results.

   3.2 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form.

   3.3 If the sample is not preserved with zinc acetate, the analysis must be started immediately. Similarly, the measurement of dissolved sulfides must also be commenced immediately.

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4. Precision and Accuracy

4.1 Precision and accuracy for this method have not been determined, but it is claimed that the iodimetric titration of the zinc sulfide is quite accurate.

5. References

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewaters, 13th Edition, pp 551-555, Method No. 228A (1971).

TEMPERATURE

STORET Number: 00010

1. Scope and Application

   1.1 This method is applicable to drinking waters and surface waters, domestic and industrial wastes, and saline waters.

2. Summary of Method

   2.1 Temperature measurements may be made with any good grade of mercury-filled or dial type centigrade thermometer, or a thermistor.

3. Comments

   3.1 Measurement device should be checked against a precision thermometer certified by the National Bureau of Standards.

4. Precision and Accuracy

   4.1 There is no acceptable procedure for determining the precision and accuracy of this test.

5. Reference

   5.1 The procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 13th Edition, p. 348, Method 162 (1971).

THRESHOLD ODOR

(Consistent Series Method)

STORET NO:
60°C: 00086
ROOM TEMP: 00085

1. Scope and Application

1.1 This method is applicable to the determination of threshold odor of finished waters, surface waters, domestic and industrial wastes, and saline waters.

1.2 Highly odorous samples are reduced in concentration proportionately before being tested. Thus, the method is applicable to samples ranging from nearly odorless natural waters to industrial wastes with threshold odor numbers in the thousands.

2. Summary of Method(1)

2.1 The sample of water is diluted with odor-free water until a dilution that is of the least definitely perceptible odor to each tester is found. The resulting ratio by which the sample has been diluted is called the "threshold odor number" (T.O.).

2.2 People vary widely as to odor sensitivity, and even the same person will not be consistent in the concentrations he can detect from day to day. Therefore, panels of not less than five persons, and preferably 10 or more, are recommended to overcome the variability of using one observer.(2)

2.2.1 As an absolute minimum, two persons are necessary: One to make the sample dilutions and one to determine the threshold odor.

3. Sample Handling and Preservation

3.1 Water samples must be collected in glass bottles with glass or Teflon-lined closures.

3.1.1 Plastic containers are not reliable for odor samples and must not be used.

3.2 Odor tests should be completed as soon as possible after collection of the sample. If storage is necessary, collect at least 1000 ml of sample in a bottle filled to the top. Refrigerate, making sure no extraneous odors can be drawn into the sample as the water cools.

4. Interferences

4.1 Most tap waters and some waste waters are chlorinated. It is often desirable to determine the odor of the chlorinated sample as well as of the same sample after removal of chlorine. Dechlorination is achieved using sodium thiosulfate in exact stoichiometric quantity.

4.1.1 It is important to check a blank to which a similar amount of dechlorinating agent has been added to determine if any odor has been imparted. Such odor usually disappears upon standing if excess reagent has not been added.

5. Apparatus

5.1 Odor-free glassware: Glassware must be freshly cleaned shortly before use, with non-odorous soap and acid cleaning solution followed by rinsing with odor-free water. Glassware used in odor testing should be reserved for that purpose only. Rubber, cork, and plastic stoppers must not be used.

5.2 Constant temperature bath: A water bath or electric hotplate capable of maintaining a temperature control of ±1°C for performing the odor test at 60°C. The temperature bath must not contribute any odor to the odor flasks.

5.3 Odor Flasks: Glass stoppered 500 ml (ST 32) Erlenmeyer flasks, or wide-mouthed 500 ml Erlenmeyer Flasks equipped with Petri dishes as cover plates.

NOTE: Narrow-mouth vessels are not suitable for running odor tests. Potential positive bias due to color and/or turbidity of water sample under observation can be eliminated by wrapping odor flasks in aluminum foil, painting flasks with non-odorous paint, or by using red actinic Erlenmeyer flasks.

5.4 Sample Bottles: Glass bottles with glass or Teflon-lined closures.

5.5 Pipets, measuring: 10.0 and 1.0 ml graduated in tenths.

5.6 Graduate cylinders: 250, 200, 100, 50, and 25 ml.

5.7 Thermometer: 0-110°C (±1°C), chemical or metal stem dial type.

5.8 Odor free water generator: See Figure 1.

6. Reagents

6.1 Odor-free water: Odor-free dilution water must be prepared as needed by filtration through a bed of activated carbon. Most tap waters are suitable for preparation of odor-free waters, except that it is necessary to check the filtered water for chlorine residual, unusual salt concentrations, or unusually high or low pH. All these may affect some odorous samples.

Where supplies are adequate, distilled water avoids these problems as a source of odor-free water. A convenient odor-free water generator may be made as shown in Figure 1. Pass tap or distilled water through the odor-free water generator at a rate of 0.1 liter/minute. When the generator is first started, it should be flushed to remove carbon fines before the odor-free water is used. The carbon cartridge,(3) or a comparable assembly, is also suitable.

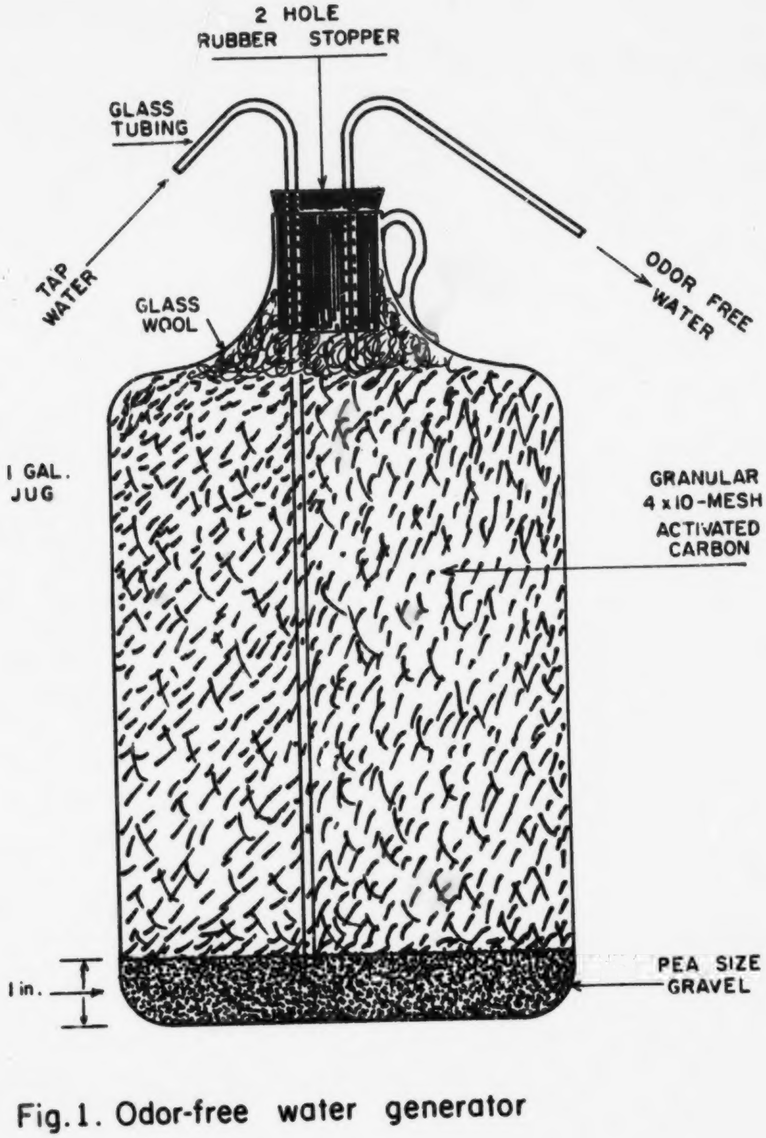
2 HOLE
RUBBER STOPPER
GLASS TUBING
TAP WATER
ODOR FREE WATER
GLASS WOOL
1 GAL. JUG
GRANULAR 4 x 10-MESH ACTIVATED CARBON
1 in.
PEA SIZE GRAVEL

Fig. 1. Odor-free water generator

6.1.1 The quality of water obtained from the odor-free water generator should be checked daily at the temperature tests are to be conducted (room temperature and/or 60°C). The life of the carbon will vary with the condition and amount of water filtered. Subtle odors of biological origin are often found if moist carbon filters are permitted to stand idle between test periods. Detection of odor in the water coming through the carbon indicates a change of carbon is needed.

7. Procedure

7.1 Precautions: Selection of persons to make odor tests should be carefully made. Extreme sensitivity is not required, but insensitive persons should not be used. A good observer has a sincere interest in the test. Extraneous odor stimuli such as those caused by smoking and eating prior to the test or through the use of scented soaps, perfumes, and shaving lotions must be avoided. The tester should be free from colds or allergies that affect odor-response. Frequency of tests must not be so great as to induce fatigue. Frequent rests in an odor-free atmosphere are recommended.

The room in which the tests are to be conducted should be free from distractions, drafts, and other odor. In certain industrial atmospheres, a special odor-free room may be required, ventilated by air filtered through activated carbon and maintained at a constant comfortable temperature and humidity(4).

For precise work a panel of five or more testers should be used. The persons making the odor measurements should not prepare the samples and should not know the dilution concentrations being evaluated. These

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persons should have been made familiar with the procedure before participating in a panel test. Always start with the most dilute sample to avoid tiring the senses with the concentrated sample. The temperature of the samples during testing should be kept within 1 degree of the specified temperature for the test.

7.2 Threshold Measurement: The ratio by which the odor-bearing sample has to be diluted with odor-free water for the odor to be just detectable by the odor test is the "threshold odor number" (T.O.). The total volume of sample and odor-free water used in each test is 200 ml. The proper volume of odor-free water is put into the flask first; the sample is then added to the water. Table 1 gives the dilutions and corresponding threshold numbers.

Table 1. Threshold Odor Number Corresponding to Various Dilutions

Sample Volume (ml) Diluted to 200 ml	Threshold Odor Number
200	1
100	2
50	4
25	8
12.5	16
6.3	32
3.1	64
1.6	128
0.8	256

7.3 Determine the approximate range of the threshold odor by:

7.3.1 Adding 200 ml, 50 ml, 12.5 ml, and 3.1 ml of the sample to separate 500 ml glass-stoppered Erlenmeyer flasks containing odor-free water to make a total volume of 200 ml. A separate flask containing only odor-free water serves as the reference for comparison. If run at 60°C, heat the dilutions and the reference in the constant temperature bath to 60°C (±1°C).

7.3.2 Shake the flask containing the odor-free water, remove the stopper, and sniff the vapors. Test the sample containing the least amount of odor-bearing water in the same way. If odor can be detected in this dilution, more dilute samples must be prepared as described in 7.3.3. If odor cannot be detected in the first dilution, repeat the above procedure using the sample containing the next higher concentration of the odor-bearing water, and continue this process until odor is clearly detected.

7.3.3 If the sample being tested requires more extensive dilution than is provided by Table 1, an intermediate dilution is prepared from 20 ml of sample diluted to 200 ml with odor-free water. Use this dilution for the threshold determination. Multiply the T.O. obtained by ten to correct for the intermediate dilution. In rare cases more than one tenfold intermediate dilution step may be required.

7.4 Based on the results obtained in the preliminary test, prepare a set of dilutions using Table 2 as a guide. One or more blanks are inserted in the series, in the vicinity of the expected threshold, but avoiding any repeated pattern. The observer does not know which dilutions are odorous and which are blanks. He smells each flask in sequence, beginning with the least concentrated sample and comparing with a known flask of odor-free water, until odor is detected with utmost certainty.

Table 2. Dilutions for Various Odor Intensities

Sample Volume in Which Odor First Noted			
200 ml	50 ml	12.5 ml	3.1 ml
Volume (ml) of Sample to be Diluted to 200 ml			
200	100	50	(Intermediate Dilution, See 7.3.3)
100	50	25	
50	25	12.5	
25	12.5	6.3	
12.5	6.3	3.1	

7.5 Record the observations of each tester by indicating whether odor is noted (+ sign) in each test flask.

For example:

ml sample diluted to 200 ml	12.5	0	25	0	50	100	200
Response	-	-	+	-	+	+	+

8. Calculations

8.1 The threshold odor number is the dilution ratio at which odor is just detectable. In the example above (7.5), the first detectable odor occurred when 25 ml sample was diluted to 200 ml. Thus, the threshold is 200 divided by 25, equals 8. Table 1 lists the threshold numbers that correspond to common dilutions.

8.2 Anomalous responses sometimes occur; a low concentration may be called positive and a higher concentration in the series may be called negative. In such a case, the threshold is designated as that point of detection after which no further anomalies occur. For instance:

ml sample diluted to 200 ml	6.3	12.5	0	25	50	100
Response	+	-	-	+	+	+
				↓ threshold		

8.3 Calculations of panel results to find the most probable average threshold are best accomplished by appropriate statistical methods. For most purposes, the threshold of a group can be expressed as the geometric mean (G.M.) of the individual thresholds. The geometric mean is calculated in the following manner:

8.3.1 Obtain odor response as outlined in Procedure and record results. For example:

Table 3. Sample Odor Series

ml of Odor-free Water	ml of Sample	Observer Response*				
		1	2	3	4	5
188	12.5	-	-	-	-	-
175	25	-	⊕	-	+	⊕
200	0	-	-	-	-	-
150	50	⊕	+	-	-	+
200	0	-	-	-	-	-
100	100	+	+	⊕	⊕	+
0	200	+	+	+	+	+

*Circled plus equals threshold level.

8.3.2 Obtain individual threshold odor numbers from Table 1.

Observer	T.O.
1	4
2	8
3	2
4	2
5	8

8.3.3 The geometric mean is equal to the nth root of the product of n numbers. Therefore:

$4 \times 8 \times 2 \times 2 \times 8 = 1024$,

and $\sqrt[5]{1024} = \frac{\log 1024}{5} = \frac{3.0103}{5} = 0.6021$,

and anti-log of 0.6021 = 4 = T.O.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

9.2 A threshold number is not a precise value. In the case of the single observer, it represents a judgment at the time of testing. Panel results are more meaningful because individual differences have less influence on the result. One or two observers can develop useful data if comparison with larger panels has been made to check their sensitivity. Comparisons of data from time to time or place to place should not be attempted unless all test conditions have been carefully standardized and some basis for comparison of observer intensities exists.

References

1. Standard Methods, 13th Edition, Amer. Public Health Asso., New York, N.Y. p. 248, Method 136 (1971).
2. ASTM, Comm E-18, STP 433, Basic Principles of Sensory Evaluation; STP 434, Manual on Sensory Testing Methods; STP 440, Correlation of Subjective-Objective Methods in the Study of Odors and Taste; Phil., Pennsylvania (1968).
3. Standard Methods, 12th Ed., Amer. Public Health Asso., New York, N.Y., 1965, p. 213.
4. Baker, R.A., "Critical Evaluation of Olfactory Measurement". Jour WPCF, 34, 582 (1962).

TURBIDITY

1. Scope and Application

1.1 This method is applicable to surface and saline waters in the range of turbidity from 0 to 40 Jackson units.

2. Summary of Method

2.1 The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings, in Jackson units, are made in a nephelometer designed according to specifications outlined in Apparatus, 5. A standard suspension of Formazin, also prepared under closely defined conditions, is used to calibrate the instrument.

2.1.1 Formazin polymer is used as the turbidity reference suspension for water because it is more reproducible than other types of standards previously used for turbidity standards.

3. Sample Handling and Preservation

3.1 Samples taken for turbidity measurements should be analyzed as soon as possible. Preservation of samples is not recommended.

4. Interferences

4.1 The presence of floating debris and coarse sediments which settle out rapidly will give false high readings. Finely divided air bubbles will also affect the results in a positive manner.

4.2 The presence of true color, that is the color of water which is due to dissolved substances which absorb light will cause turbidities to be low, although this effect is generally not significant with finished waters.

5. Apparatus

5.1 The turbidimeter shall consist of a nephelometer with light source for illuminating the sample and one or more photo-electric detectors with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. The turbidimeter should be so designed that little stray light reaches the detector in the absence of turbidity and should be free from significant drift after a short warm-up period.

5.2 The sensitivity of the instrument should permit detection of turbidity differences of 0.02 unit or less in waters having turbidities less than 1 unit. The instrument should measure from 0 to 40 units turbidity. Several ranges will be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities.

5.3 The sample tubes to be used with the available instrument must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched. They must not be handled at all where the light strikes them, but should be provided with sufficient extra length, or with a protective case, so that they may be handled.

5.4 Differences in physical design of turbidimeters will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, the following design criteria should be observed:

5.4.1 Light source: Tungsten lamp operated at not less than 85% of rated voltage or more than rated voltage.

5.4.2 Distance traversed by incident light and scattered light within the sample tube: Total not to exceed 10 cm.

5.4.3 Angle of light acceptance of the detector: Centered at 90° to the incident light path and not to exceed ±30° from 90°.

5.4.4 Maximum turbidity to be measured: 40 units.

5.5 At the time of this writing, the only instrument commercially available with these specifications is the Hach Turbidimeter, Model 2100 and 2100A. This instrument is recommended.

6. Reagents

6.1 Turbidity-free water - Pass distilled water through a 0.45 μ pore size membrane filter if such filter and water shows a lower turbidity than the distilled water.

6.2 Stock turbidity suspension:

Solution 1: Dissolve 1.00g hydrazine sulfate, $(HN_2)_2.H_2SO_4$, in distilled water and dilute to 100 ml in a volumetric flask.

Solution 2: Dissolve 10.00g hexamethylenetetramine in distilled water and dilute to 100 ml in a volumetric flask.

In a 100-ml volumetric flask, mix 5.0 ml Solution 1 with 5.0 ml Solution 2. Allow to stand 24 hours at 25 ± 3°C, then dilute to the mark and mix.

6.3 Standard turbidity suspension: Dilute 10.00 ml stock turbidity suspension to 100 ml with turbidity-free water. The turbidity of this suspension is defined as 40 units. Dilute portions of the standard turbidity suspension with turbidity-free water as required.

6.3.1 A new stock turbidity suspension should be prepared each month. The standard turbidity suspension and dilute turbidity standards should be prepared weekly by dilution of the stock turbidity suspension.

7. Procedure

7.1 Turbidimeter calibration: The manufacturer's operating instructions should be followed. Measure standards on the turbidimeter covering the range of interest. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration scales. At least one standard should be run in each instrument range to be used. Some instruments permit adjustments of sensitivity so that scale values will correspond to turbidities.

Reliance on a manufacturer's solid scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges. If a pre-calibrated scale is not supplied, then calibration curves should be prepared for each range of the instrument.

7.2 Turbidities less than 40 units: Shake the sample to thoroughly disperse the solids. Wait until air bubbles disappear then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

7.3 Turbidities exceeding 40 units: Dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor. For example, if 5 volumes of turbidity-free water were added to 1 volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample was 180 units.

7.3.1 The Hach Turbidimeters, Models 2100 and 2100A, are equipped with 5 separate scales: 0-.02, 0-1.0, 0-10.0, 0-100, and 0-1000 JTU. It is strongly recommended, however, that the upper scales be used as indications of required dilution volumes to reduce readings to less than 40 JTU. (NOTE: Comparative work performed in the AQC Laboratory indicates a progressive error on sample turbidities in excess of 40 units.)

8. Calculation

8.1 Multiply sample readings by appropriate dilution to obtain final reading.

8.2 Report results as follows:

Jackson Turbidity Units	Record to nearest:
0.0-1.0	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1000	50
>1000	100

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

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